# APPENDIX G
# ILLINOIS RIVER HISTORICAL REPORT

# Phosphorus Retention and Sediment-Phosphorus Interactions in Point-Source-Impacted Ozark Streams

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## INTRODUCTION

Water quality is a central concern for meeting the needs of an ever-increasing population in Northwest Arkansas. Despite substantial improvement in water quality following the Clean Water Act (Sharpley et al., 1994), the quality of our nation's waters is still being degraded by point and nonpoint sources of pollution (U.S. EPA, 2000). Discrete or point source (PS) dischargers are readily identifiable and may be channels, pipes, or conduits that aid in transporting pollutants such as the outfall from municipal wastewater treatment plants (WWTPs). Nonpoint sources (NPS) or diffuse sources do not have a defined discharge point; nutrient loading in surface runoff from the urban landscape, pasturelands and other agricultural activities are examples of NPS pollution. Excessive nutrient inputs (especially phosphorus, hereafter referred as P) from PS and NPS pollution accelerate the natural process of eutrophication, thus potentially impairing designated beneficial uses of surface waters (Carpenter et al., 1998).

Almost 15% of rivers and streams in Arkansas have been identified as impaired for their designated uses (U.S. EPA, 2000). The total P (TP) criterion recommended by United States Environmental Protection Agency (U.S. EPA) is 0.1 mg $L^{-1}$ for streams and rivers and 0.05 mg $L^{-1}$ for lakes in Arkansas (U.S. EPA, 2003). Recently, the Arkansas Department of Environmental Quality (ADEQ) also indicated that about 15% of the state's assessed streams do not meet their designated uses because of elevated nutrient concentrations (ADEQ, 2002).

The Illinois River Basin is a trans-boundary watershed between Arkansas and Oklahoma (Figure 1.1) and has recently been the subject of political and environmental debate due to nutrient enrichment and accelerated eutrophication in some Scenic Rivers of Oklahoma. In 1992, a U.S. Supreme court ruling suggested that the U.S. EPA may require upstream states to adhere to downstream states' water quality standards. The Illinois River and Flint Creek, which flow from Northwest Arkansas into Northeast Oklahoma, have been listed as Scenic Rivers in Oklahoma and, therefore, are subject to TP criterion of 0.037 mg $L^{-1}$ established by the Oklahoma Water Resources Board (OWRB, 2002). The average flow-weighted TP concentration at the Illinois River near the Arkansas-Oklahoma border was approximately 0.40 mg $L^{-1}$ (Green and Haggard, 2001), over ten times greater than the TP criterion suggested by OWRB.

**Figure 1.1.** The Illinois River Basin, a trans-state watershed between Arkansas and Oklahoma with major cities and rivers. The Illinois River originates from Northwest Arkansas and flows into Northeast Oklahoma.

Nonpoint sources of pollution have been the focus of a great deal of water resources research in the Ozark Plateaus as well as in other areas of the United States. Arkansas is a leading poultry producer in the United States with an output of over one billion broilers each year (Arkansas Agricultural Statistics Service, 1996). Poultry litter is often land-applied as a fertilizer to agricultural and pasture lands. Edwards and Daniel (1993a) showed that 2% to 7% of TP in poultry litter can be lost in surface runoff, a high proportion (80% to 95%) of which was in the dissolved form. Dissolved reactive P (DRP) loss from soil and land-applied poultry litter may transport large amounts of P into streams and rivers. Phosphorus often acts as a limiting nutrient for algal growth in streams, so the elevated P concentrations at the Illinois River and some other Scenic Rivers of Oklahoma are the main concern. Recently, Vieux and Moreda (2003) suggested that best management practices (BMPs) on the Arkansas side could help alleviate the substantial portion of P transport resulting from land-applied poultry litter in the Illinois River Basin.

However, Vieux and Moreda (2003) did not include P loading from municipal WWTPs, which is a significant part (45%) of total P loadings at the Illinois River Basin (Haggard et al., 2003). Haggard et al. (2003) showed that municipal WWTPs were the major contributor to elevated P concentrations during base flow conditions, in Northwest Arkansas. These elevated P concentrations in the Illinois River near the Arkansas-Oklahoma border were traced to one municipal WWTP over 45 km upstream, demonstrating the pronounced impact of WWTPs in the basin (Haggard et al., 2003).

Several other researchers have demonstrated the impact of municipal WWTPs on the P concentrations in streams and sediments (e.g., Dorioz et al., 1998; House and Denison, 1997). Investigations have focused on whole-reach P retention, as well as specific mechanisms of P retention such as sediment-P buffering capacity and the amount of P in sediments (Haggard et al., 2001a; Dorioz et al., 1998; House and Denison, 1997; Reddy et al., 1996). P retention efficiency or adsorption capacity, of Ozark streams was reduced downstream from WWTPs, and the amount of P from WWTP inputs was significant in determining the degree of impact (Haggard et al., 2004). Stream sediments may play a major role in regulating P concentrations in the water column, especially when residence time of water is longer, i.e., under baseflow conditions (Svendsen et al., 1995; Fox et al., 1989). The affinity of dissolved inorganic P for sediments results in the important processes of adsorption and desorption, thus controlling P concentrations in freshwaters (Sharpley et al., 2002). The ability of sediments to retain P in streams receiving municipal WWTPs discharge has been found to be less than that in streams draining lands with extensive pastures and animal agriculture (Popova, 2000).

Both nutrient retention and sediment-P interactions influence P uptake, transport and transformation in stream systems. Thus, there is a need to investigate stream P retention and sediment-P interactions in streams of the Illinois River Basin receiving municipal WWTP effluent. This investigation could yield important information to watershed managers on elevated P concentrations and deteriorating water quality due to municipal WWTPs. These PS may further degrade water quality if left unaddressed, particularly in basins where P loads are elevated above eutrophic levels.

Based on the previous findings that WWTPs significantly affect the P concentrations in receiving streams, it was hypothesized that (i) P enrichment due to effluent from municipal WWTPs in headwater streams of the Illinois River has resulted in elevated water column soluble reactive P (SRP) and sediment-bound P in these stream ecosystems, (ii) dilution due to groundwater and lateral contributions, and not assimilation, is responsible for decreasing SRP concentration longitudinally downstream, and (iii) the relationship between water column SRP and sediment-bound P are the controlling mechanisms of P concentrations in stream systems.

**Objectives:**

The overall goal of this study was to evaluate whole-stream P retention in four Ozark streams receiving effluent from municipal WWTPs with varying degrees of P enrichment. In order to accomplish this goal, the following objectives were identified:

(1)  Compare the SRP concentrations in the water column and stream sediments between reference sites (upstream) and sites downstream from the WWTP inputs;
(2)  Examine longitudinal variation in SRP and $Cl^-$ concentrations (if any) downstream of WWTP inputs to determine if assimilation rather than dilution is responsible for net P retention;
(3)  Conduct smaller-scale investigations to evaluate the ability of sediments to adsorb or release P by measuring easily exchangeable P (EXP), P sorption index (PSI), and equilibrium P concentration ($EPC_0$) in benthic sediments.

# LITERATURE REVIEW

**Stream Water Quality and Phosphorus**

Ecosystems and ecological services

Directly or indirectly, humans derive many valuable benefits such as water supply, waste treatment, recreation, and refugia from ecological systems (Constanza et al., 1998). The ecosystem goods (e.g., food) and services (e.g., waste assimilation) can together be referred to as the ecological services (Table 2.1). Concerns have increased on issues relating to stream water quality, and the ecological services and biodiversity provided by these stream ecosystems. Natural resources should be managed carefully to obtain long-term benefits of these ecological services because they are critical to human welfare (Lackey, 1998). Although substantial improvements in water quality have been made in last 30 years, pollution still remains a threat to our nation's waters (U.S. EPA, 2000). The recovery of aquatic ecosystems from a eutrophic state is a gradual process often requiring many years and remediation techniques that may be overly expensive, especially if implementation is delayed (Sharpley et al., 1994; Carpenter et al., 1998; Daniel et al., 1998).

**Table 2.1.** Ecological services related to water quality. These include only renewable ecological services, excluding the non-renewable fuels, minerals, and the atmosphere (modified from Constanza et al., 1998).

| Ecological Service | Role/function of Ecological Service |
|---|---|
| Water regulation | Regulating the hydrological flow for irrigation purpose and industrial processes |
| Water supply | Storage and retention of water in aquifers and reservoirs |
| Soil erosion control and sediment retention | Preventing soil loss from an ecosystem |
| Nutrient cycling | Cycling and assimilation of nutrients e.g., nitrogen fixation that aids in plant growth |
| Waste treatment/assimilation | Streams may act as "self-purifiers" on a spatial basis breaking down nutrients and complex pollutants such as heavy metals |
| Habitat | Provides a habitat for permanent and migratory species of benthic macro invertebrates, and fish that are integral part of an aquatic ecosystem |
| Recreational purposes | Swimming, fishing, and other outdoor recreational activities |
| Cultural purposes | Aesthetic, educational and scientific value |

Eutrophication and associated problems

Eutrophication is the high production of biota in aquatic ecosystems often associated with over-enrichment of nutrients such as phosphorus (P) (Wetzel, 2001). Eutrophication (Figure 2.1) of aquatic ecosystems may be accelerated by human activities and has become a problem associated with stream water quality and ecological integrity. A commonly associated problem with stream eutrophication and nutrient enrichment may be augmented algae growth in streams, which results in large diurnal fluctuations in dissolved oxygen and pH, potentially leading to fish-kills (Biggs, 1985; Correll, 1998). Acceleration of the natural process of eutrophication may impair designated beneficial uses of surface waters (Sharpley et al., 1994; Carpenter et al., 1998; Sharpley et al., 2002) such as swimming, fishing, industrial water supply and other purposes (Biggs, 1985; Carpenter et al., 1998). The significant role of P enrichment in freshwater eutrophication has been discussed widely by several researchers with suggestions to control the export of P into streams (Daniel et al., 1998; Correll, 1998; Parry, 1998). In contrast, Jarvie et al. (2002) showed that algal blooms and biofilm production in riverine systems is positively related to light exposure and decline in discharge rather than P availability.

Eutrophication is a dynamic process, making it fairly complex to understand because aquatic ecosystems may behave quite differently having different P retention characteristics based on seasonal and interannual variations. Researchers have used various approaches, such as intensive monitoring of water quality and watershed-scale modeling, to attempt to solve the problem and maintain healthy aquatic ecosystems for future generations.



**Figure 2.1.** Illustration of eutrophication at Lake 227, excessive P caused bright green color. Lake 305 in the background is undisturbed (University of Manitoba's Experimental Lakes Area, 1994).

Increasing concerns for management of water pollution led to the enactment of the Federal Water Pollution Control Act Amendment in 1972 that was revised in 1977 as the Clean Water Act. The objective of the Clean Water Act was to protect the physical, chemical, and biological integrity of surface waters in the U.S. (Gallagher and Miller, 1996). The United States Environmental Protection Agency (U.S. EPA) was given the responsibility of helping states set their water quality standards, in addition to its national role. In the most recently published data, 39% of the total stream and river miles of the U.S. have been designated as impaired for one or more uses (U. S. EPA, 2000). The U.S. EPA is continuously seeking new techniques, e.g., developing total maximum daily loads (TMDLs), to address these issues of water quality impairment. Parry (1998) and Sharpley et al. (2002) have suggested that a coordinated effort of skill and resources from all segments of society is required to achieve the objectives of the Clean Water Act.

Federal and state agencies other than U.S. EPA, such as the Arkansas Department of Environmental Quality (ADEQ), are also actively involved in setting, evaluating and achieving water quality standards to accomplish the objectives of the Clean Water Act. A large percentage of streams and rivers in the Ozark highlands of Arkansas have been designated as extraordinary resource waters. Recently, ADEQ reported that 15% of the almost 90,000 river and stream miles in Arkansas are not meeting their designated uses (ADEQ, 2002).

**Nonpoint Sources and Point Sources of Pollution**
The potential reasons for degradation of water quality may be nutrient loadings from agricultural run-off, urban parking lots, and ineffective municipal wastewater treatment plants (WWTPs). The main causes for water pollution have been classified broadly as – nonpoint sources and point sources. These sources contribute P to streams in different forms and amounts. Excess inputs of P are a major cause of surface water impairment in the United States (Sharpley et al., 1994; U.S. EPA 1990, 1996; Carpenter et al., 1998), and Arkansas (U.S. EPA, 2000).

Nonpoint sources of phosphorus
Nonpoint sources (NPS), or diffuse sources, usually elevate nutrient loading when surface runoff occurs, e.g., nutrient loadings from pastures, agricultural fields, and urbanization. Nonpoint sources of pollution are ubiquitous and often expensive to control. Agricultural activities have been identified as major NPS of P to the freshwater ecosystems. Many efforts have been made in the United States to understand the impact of various NPS of pollution on stream systems. However, watershed managers still need to enhance their understanding of P transport, especially from NPS to devise more efficient management strategies (Svendsen et al., 1995; Daniel et al., 1998).

Influence of land use on stream P
In nonpoint pollution of surface waters a major source of P results primarily from agriculture and urbanization (Carpenter et al., 1998). Several studies have shown increases in P concentration and export in streams with an increase in proportion of agricultural land use or pasture within a catchment (Edwards et al., 1996; Cooke and Prepas, 1998; McFarland and Hauck, 2001; Haggard et al., 2003a). For example, in a

Central Texas watershed, 48% of P export was from dairy waste application fields (McFarland and Hauck, 2001). Phosphorus from agriculturally-dominated watersheds elevates stream water column P as well as the amount of P in sediments (Reddy et al., 1996; Popova, 2000). Some studies have suggested urbanization as a significant factor increasing P concentrations and export to streams (Dillon and Kirchner, 1975; Osborne and Wiley, 1988). In a modeling approach, Soranno et al. (1996), predicted that transformation of undisturbed lands to urbanized and agricultural land can elevate P loads to aquatic ecosystems. The range of P export from agricultural, forest, and urban land use is 0.5 to 2.5, 0.2 to 1.5, and 1.1 to 16.6 kg ha$^{-1}$ yr$^{-1}$, respectively (Dillon and Kirchner, 1975; McFarland and Hauck, 2001). The form of P exported from agricultural lands and pastures is generally in the dissolved inorganic form, and several studies have shown that dissolved form of P represents more than 80% of the TP export from both agriculture and pasture land use (Edwards and Daniel, 1993b; Cooke and Prepas, 1998).

P concentrations in streams were more strongly related to overall watershed characteristics than stream-side vegetation proximity (Omernik et al., 1981). However, Johnson et al. (1997) found that more than 40% of the variance in P concentrations could be explained by riparian width, as well as the whole-catchment landscape characteristics. Recently, Franklin et al. (2002) showed that dissolved P in streams was not related to morphological characteristics of the watershed such as stream order, drainage density, contributing area, and stream length.

NPS has been the focus in Ozarks

Poultry litter is a rich source of nutrients and is often land-applied as an organic fertilizer. Because of extensive poultry farms in the Ozark highlands of Northwest Arkansas and use of poultry litter on pastures, the effect of poultry litter applications on P loss from the landscape has been a primary focus for the last decade. Several studies have shown increased P concentration in runoff water (where 2% to 7% of P applied is lost in surface runoff) from plots receiving poultry litter (Edwards and Daniel, 1993a; 1993b). Although increases in rainfall intensity may dilute TP and dissolved P concentrations in runoff from small plots, net P loss increased with an increase in rainfall intensity (Edwards and Daniel, 1993a). They also reported that an increase in the application rate of poultry litter increases both P concentrations and net mass losses from small plots during rainfall simulation studies. Poultry litter is a greater source of P loss in runoff as compared to excretions from grazing animals (Sauer et al., 1999). Poultry litter application also increases the amount of plant available P in the surface layers of soil (Kingery et al., 1994). Studies have often evaluated the relation between P concentrations and found a strong positive relation in runoff water and soil test P in small plots (e.g., Pote et al., 1999a; 1999b).

The tendency to focus on only a single class of sources in Northwest Arkansas has resulted in blaming only NPS and ignore the contribution of PS such as WWTPs to nutrient loading. Clearly, the most comprehensive strategy would be to consider all sources of P in a watershed management program.

Point Sources of Phosphorus

Point sources (PS) or discrete sources of pollution are an identifiable source of P loading to streams e.g., municipal WWTPs, urban parking lots, and concentrated animal

feeding operations (CAFOs). Section 502 of the Clean Water Act defines PS as "any discernable, confined and discrete conveyance from which pollutants may be discharged and includes but is not limited to any pipe, ditch, channel, and CAFOs. Point sources are required to have a National Pollutant Discharge Eliminations System (NPDES) permit to discharge to the waters of the U.S. As an exception, CAFOs are the only agricultural source required to have this permit (Parry, 1998).

Impact of municipal WWTPs on aquatic ecosystems

Municipal WWTP inputs can augment P loading to streams and can have several adverse effects on the aquatic ecosystem. For example, fish diversity was severely affected up to 54 km downstream from a WWTP outfall and species richness of the benthic macro-invertebrates gradually recovered approximately 14 km below the WWTP outfall (Birge et al., 1989). Municipal WWTP effluent caused sediment deoxygenation and increased biochemical oxygen demand (BOD) up to 20 km downstream from the outfall, somewhat contradicting the concept of "self-purification" in streams (Rutherford et al., 1991). The distance required to temporarily retain over 63% of WWTP inputs has been reported to be up to 30 km (Haggard et al., 2001a; Marti et al., 2003). Municipal WWTP effluent with high P can increase the amount and availability of P in stream bottom sediments (Chambers and Prepas, 1994; Haggard et al., 2001a). Dorioz et al. (1998) also demonstrated that river sediments have two-fold greater P content downstream from municipal WWTPs as compared to sediments in streams draining agricultural dominated watersheds (see also Popova, 2000). Recent studies have also shown that municipal WWTPs substantially reduce stream P retention efficiency (Haggard et al., 2001a; 2004; Marti et al., 2003).

Municipal WWTPs contribute more than 50% of P reaching rivers from urban areas (Carpenter et al., 1998). Even in the Ozark highlands, municipal WWTPs are a major contributor to stream P concentrations and loads (Nelson et al., 2002; Haggard et al., 2003). In an Ozark catchment, average annual TP load at the Illinois River near Arkansas-Oklahoma border is about 208,000 kg, where 45% of the annual loading is from municipal WWTPs (Haggard et al., 2003b). Up to 83% of the average annual P loading from municipal WWTPs in the Illinois River can be attributed to a single WWTP (Nelson et al., 2002) and elevated dissolved P concentration could be traced over 40 km upstream to this WWTP (Haggard et al., 2003). Municipal WWTPs in Northwest Arkansas have no regulatory limits on the effluent concentrations with only few exceptions such as the City of Fayetteville WWTP. Recently, cities of Rogers and Springdale municipal WWTPs have set voluntary effluent limits (personal communication with Mike Lawrence and Jennifer Enos at Rogers and Springdale municipal WWTPs, respectively).

**Phosphorus Spiraling**

Spiraling concept

        Streams have the ability to transport, retain, and a capacity to sustain a degree of P loading (Stream Solute Workshop 1990). Stream retention efficiency may be reduced substantially due to high P loads, thus affecting the gradient of P concentration and downstream water quality. Therefore, knowledge of fate and transport of P molecules in streams is important in further understanding P retention, spiraling, and subsequent water quality problems. Phosphorus exchanges from the water column to the stream benthos include biotic components such as microbial community (Gatcher and Meyer, 1993; Webster et al., 1991) and aquatic macrophytes (Chambers and Prepas, 1994; Pelton et al., 1998), and abiotic components such as sediments (Meyer, 1979; Hill, 1982; Klotz 1988).

        Phosphorus cycling in the streams involves downstream displacement of a P molecule during a cycle and has been called "spiraling" (Webster and Patten, 1979; Newbold et al., 1981). Spiraling length (S) is the average distance traveled by a P molecule when completing a cycle from the dissolved inorganic form in the water column into the particulate form after uptake by the stream benthos and then back into the dissolved inorganic form in the water column (Figure 2.2).



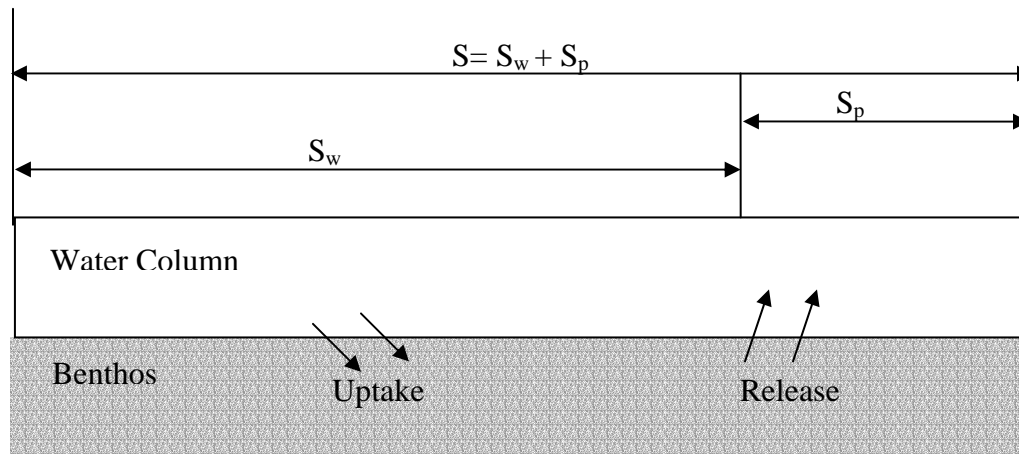**Figure 2.2.** Nutrient spiraling model (Adapted from: Newbold, 1992). Spiraling length (S) is the distance a P molecule would travel downstream. S is the sum of the distance a P molecule travels in the water column in dissolved inorganic form ($S_w$) until its uptake by the benthos. $S_p$ is the distance the P molecule would travel in particulate form until released back into the water column in dissolved inorganic form.

Spiraling length (S) is the sum of the uptake length ($S_w$) and the turnover length ($S_p$) (Newbold et al., 1983). $S_w$ is the average distance traveled by a P molecule while in dissolved inorganic form before being immobilized, and $S_p$ is the distance traveled in particulate form before being released back into the water column in dissolved inorganic form (Newbold et al., 1983). Newbold et al. (1983) also found that $S_w$ typically constitutes more than 90% of the spiraling length, and $S_w$ has been used as a measure of a stream's P retention efficiency. Thus, streams with shorter $S_w$ would have a greater retention efficiency than streams with longer $S_w$. $S_w$ has also been used as a measure of a streams ability to temporarily retain P supplied from the surrounding watershed (Newbold et al., 1981). Determination of $S_w$ is simple and is usually estimated using short-term solute injections; however, elemental isotopes are needed to determine $S_p$.

Conservative and non-conservative solutes

Solutes in a stream can be classified as either conservative or non-conservative based on biological and chemical reactivity (Stream Solute Workshop, 1990). Non-conservative solutes are influenced by biotic and abiotic processes within a stream. However, a conservative solute is not dependent upon biotic and abiotic processes occurring within the stream environment. Solute exchanges between the water column and stream substrate make non-conservative solute dynamics more complex in nature. Selection of a conservative solute is critical especially in stream systems where dilution may occur due to groundwater or lateral contributions (Bencala et al., 1987). Chloride ($Cl^-$) is often used as a hydrologic tracer for dilution correction, especially in stream systems, to observe the gradual downstream declines in P concentrations during short-term P additions (Stream Solute Workshop, 1990). In other streams receiving WWTP outfall, boron (B) has been suggested as a conservative tracer (Neal et al., 1998), as well as $Cl^-$ (Marti et al., 2003).

Solute transport in a stream can be affected by various factors such as species transformations, abiotic processes and biotic processes (Allan, 1995). The Stream Solute workshop (1990) widely discussed solute dynamics in streams (Figure 2.3). Solute dynamics was defined as the spatial and temporal patterns of dissolved material transport in water. The Spiraling Concept couples the principles of solute dynamics and downstream transport in fluvial ecosystems (Stream Solute workshop, 1990).
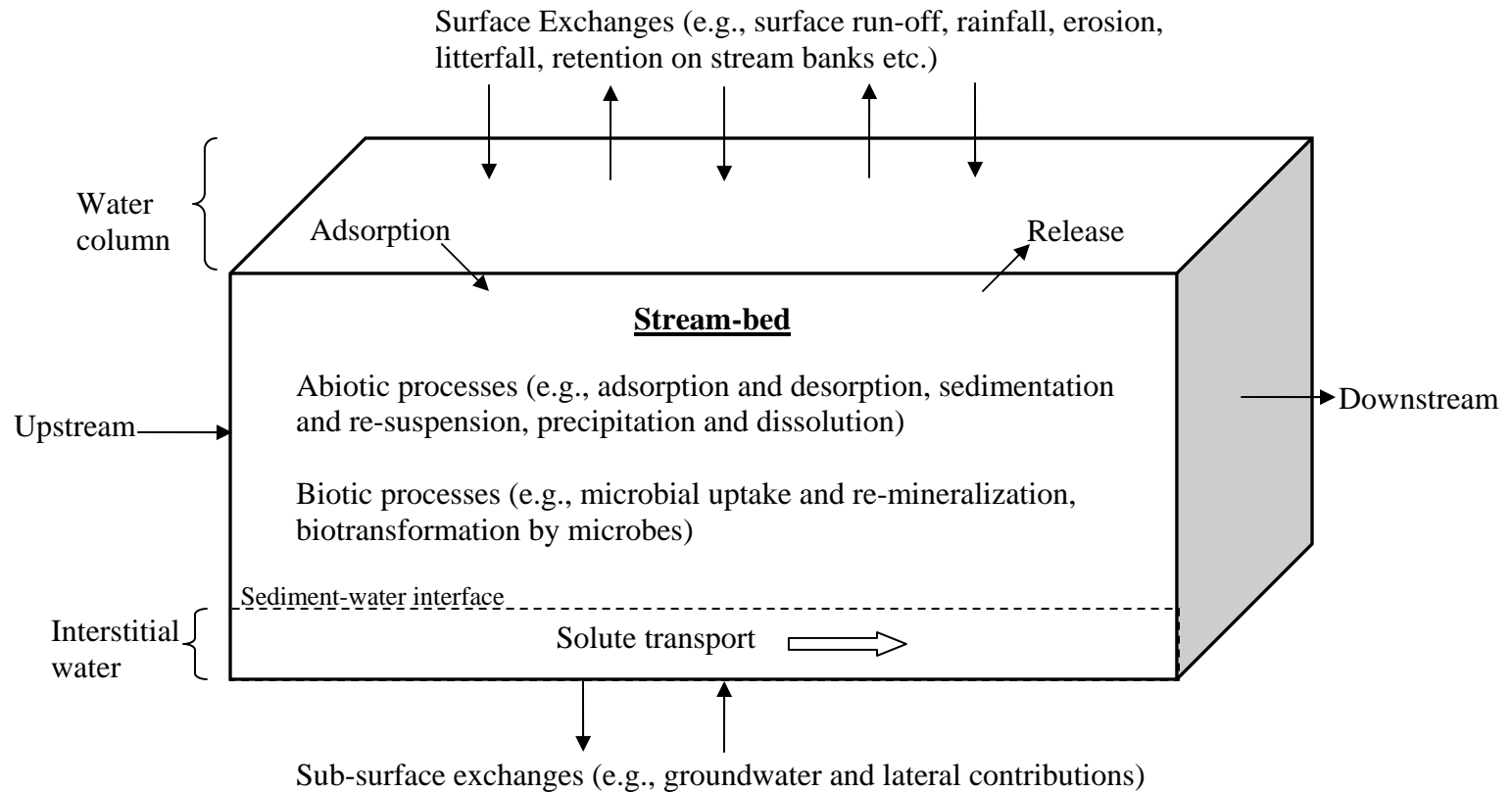
**Figure 2.3.** Conceptual diagram of solute processes in streams (Adapted from: Stream Solute Workshop, 1990; Allan, 1995).

Haggard et al. (2001a) proposed measuring whole-reach net retention ($S_{net}$) in WWTP impacted streams, based on the metrics defined within the Spiraling Concept (Stream Solute Workshop, 1990). SRP concentration decreases exponentially with increasing distance and can mathematically be expressed as:

$$C_x = C_o e^{-kx} \tag{2.1}$$

$$\ln(C_x/C_o) = -kx \tag{2.2}$$

where $C_x$ is the background and dilution-corrected SRP concentration (mg $L^{-1}$) at a distance x (km) from the WWTP effluent, $C_o$ is the background-corrected SRP concentration (mg $L^{-1}$) at first downstream site of WWTP effluent, and k is the SRP change coefficient ($km^{-1}$). $S_{net}$ is the inverse of the slope of the regression line relating natural logarithm of proportion of dilution-corrected SRP concentrations in the water column and downstream distance from the nutrient source, e.g., the WWTP input (equation 2.2). Therefore,

$$S_{net} = 1/(slope) = -1/k \tag{2.3}$$

While $S_w$ reflects gross P uptake, $S_{net}$ reflects net uptake that is, gross uptake minus the P released or regenerated within a stream reach. Several researchers have measured $S_w$ using short-term solute injection techniques under different hydrological and watershed characteristics, where $S_w$ varied from less than 0.1 to 3 km (Newbold et al., 1983; Mulholland et al., 1985; Webster et al., 1991; Marti and Sabater, 1996; Butturni and Sabater, 1996; Davis and Minshall, 1999; Haggard et al., 2001b). Recently, the distance required to assimilate 63% of P added to a stream has been used to estimate $S_{net}$, particularly in streams receiving a source of continuous P loading from WWTPs (Haggard et al. 2001b; Marti et al. 2003). The magnitude of $S_{net}$ was usually much greater than $S_w$ for dissolved P ranging from 0.1 to 31 km (Haggard et al. 2001b; Marti et al. 2003).

**Phosphorus retention in streams**

The River Continuum Concept suggests that stream systems can act as a sink or source of nutrients (P, N, C) effecting downstream water quality (Vannote et al., 1980). The transport, retention and assimilation of P in stream ecosystems are a function of physical, chemical, and biological processes (Stream Solute Workshop, 1990). Streams are characterized by unidirectional flow and a high flushing rate giving them a unique process of nutrient cycling (Essington and Carpenter, 2000).

Stream channel morphology, bed roughness and permeability may potentially control P transport and retention downstream (Triska et al., 1989; Marti and Sabater, 1996; Doyle et al., 2003). These hydrologic and geomorphologic (hydrogeomorphologic) factors enhance P retention in streams, likely from increases in P retention within the hyporheic zone (Triska et al., 1989). This hyporheic zone is where surface and subsurface water mix, and is an active region of biological activity in streams (Allan, 1995). The hyporheic zone along with deep pools constitutes the transient storage zones where movement of P and water is reduced relative to the average water velocity. Low flow conditions in streams increases the residence time of water allowing increased adsorption by stream-bed sediments, which is an important mechanism for P retention (Hill, 1982; Klotz, 1988; Svendsen et al., 1995; Reddy et al., 1996). More than 90% of P (in SRP

form) removed during stream transport under low flow conditions has been attributed to sediment sorption (Hill, 1982; Hart et al., 1992).

In small headwater streams, Meyer and Likens (1979) observed only short-term P retention and negligible annual P retention, where greater temporary P retention occurred during periods of low stream flow. Other studies have observed greater P retention efficiency (or shorter $S_w$) as stream flow decreased (Marti and Sabater, 1996; Butturini and Sabater, 1998; Haggard et al, 2001b). However, increased water velocity in streams during periods of increased stream flow increases the rate of P transfer from water column to stream sediments potentially increasing P adsorption (House et al., 1995). Thus, both flow rate and stream sediments are important in the process of P assimilation and retention in fluvial ecosystems (Munn and Meyer, 1988; Reddy et al., 1996).

Benthic sediments may play a significant role in controlling dissolved inorganic P concentrations in streams (Meyer, 1979; Froelich, 1988; Klotz, 1985; 1988; House and Warwick, 1998). Typically, stream sediments control dissolved inorganic P concentrations by maintaining an equilibrium condition with the water column, generally termed as the sediment equilibrium phosphorus concentration ($EPC_0$) (Taylor and kunishi, 1971; Froelich, 1988; Klotz, 1988). $EPC_0$ is the ambient dissolved inorganic P concentration at which there is no net adsorption or release of inorganic P from sediment. Generally, if sediment $EPC_0$ is less than the dissolved inorganic P in water column, then sediments would retain P or be a sink. In contrast, if the water column P concentration is less than the sediment $EPC_0$, a release of P may occur from sediments to approximately maintain the equilibrium. Many studies have shown a positive relation between sediment $EPC_0$ and water column P concentrations (Meyer, 1979; Klotz 1988) whereas other studies did not observe equilibrium between the water column and stream sediments (Klotz, 1985; Haggard et al., 1999).

$EPC_0$ is shown to be primarily influenced by physical processes (Klotz, 1988; Baldwin, 1996) but investigators should not neglect the potential influence of biotic factors. Particle size distribution may be an important factor controlling the rate of P sorption by sediments, where fine grained sediments have greater P sorption capacity (Meyer 1979; Hill, 1982; Klotz 1985). For example, Haggard et al. (1999) found that $EPC_0$ was significantly correlated with percent silt in benthic sediments. Exchangeable Al, Fe and $Ca^{2+}$ may also influence sediment P sorption where P sorption increases with an increase in the amount of exchangeable Al, Fe, and $Ca^{2+}$ (Meyer, 1979). In another study, Klotz (1988) found $EPC_0$ was negatively correlated with exchangeable Fe, Al, and $Ca^{2+}$. Sediment-P sorption also increases with an increase in organic matter content in sediments (Meyer, 1979; McDowell and Sharpley, 2001). The concentration of DO also influences sediment-P adsorption and release, especially in the hypolimnion of reservoirs and lakes (Kim et al., 2003). When DO is not present in sediment-water interstitial spaces, redox conditions shift to reducing conditions where P release from sediments often occurs (Kim et al., 2003) and sediment $EPC_0$ may increase more than two-fold (House and Denison, 2000). pH also influences sediment $EPC_0$, where $EPC_0$ is minimum at pH conditions near neutral, and increases as pH deviates from neutral conditions

(Klotz, 1988; Kim et al., 2003). Thus, it is clear that sediment-P sorption and $EPC_0$ are influenced by many physico-chemical factors.

Several studies have measured the P buffering capacity of stream sediments to assess the influence of abiotic and biotic processes on P retention (e.g., see Meyer 1979; Klotz, 1985; Haggard et al., 1999). Haggard et al. (1999) found that 38% of P removal could be attributed to the biological processes. In contrast, relatively low percentages were reported by Meyer (1979) and Klotz (1985). Thus, sediment-P sorption is important in P retention in streams, but biotic processes are equally important (House and Denison, 1997; McDowell and Sharpley 2003). Phosphorus may act as a limiting nutrient for detrital processing in streams (Elwood et al., 1981). Phosphorus uptake by the microbial community (Gatcher and Meyer, 1993), algae (Jarvie et al., 2002), bryophytes (Meyer, 1979), and other aquatic vegetations such as macrophytes (Chambers and Prepas, 1994; Reddy et al., 1996; Pelton et al., 1998) may play a significant role in P retention in streams. Benthic algae and vegetation have been shown to be a temporary sink for P (Hill, 1982; Reddy et al., 1996). Pelton et al. (1998) found that both macrophytes and epiphytes were important in P uptake from the water column; however, epiphytes have a greater P uptake rate compared to macrophytes. Marti and Sabater (1996) showed that algal uptake influenced $PO_4$ retention in stream reaches where light was not a limiting factor.

**Justification for using SRP**

The soluble reactive P is the form most easily available for biotic uptake. There have been contradicting ideas about measuring SRP or TP in streams, and most researchers have used SRP as a surrogate for TP even in low P conditions (Dodds, 2003). However, measuring SRP is appropriate in P-enriched systems (SRP>0.1 mg $L^{-1}$) such as a system receiving sewage effluent (Dodds, 2003). Under baseflow conditions and elevated P loadings, SRP is about 70% to 95% of the total P (Reddy et al., 1996; Jarvie et al., 2002).

# MATERIALS AND METHODS

**Study Site**

The focus of my study was on the Illinois River Basin and, specifically, four of its headwater streams in Northwest Arkansas that receive effluent from municipal wastewater treatment plants (WWTPs). The Illinois River and its tributaries are a model representation of the streams for the central United States (Brown and Matthews, 1995). The southwestern Ozark streams fall in the mid-continent region (region-4) of conterminous United States based on variations of longitudinal patterns of channel form succession. The headwater streams of this region are unique because of their uniformly spaced alluvial gravel, riffle-pool geomorphology (Brussock et al., 1985). The Illinois River Basin is dominated by karst, cherty-limestone topography with associated sandstones and shale. White et al. (2002) estimated the land use of Illinois River Basin in Arkansas as 58% pasture, 36% forest, and 6% urban.

I selected reaches at Mud Creek, Osage Creek, and Spring Creek, which are headwater streams of the Illinois River Basin, and receive WWTP effluent from the cities of Fayetteville, Rogers, and Springdale in Northwest Arkansas, respectively (Figure 3.1). The fourth stream reach was at Sager/Flint Creeks which receive WWTP effluent from Siloam Springs, Arkansas (Figure 3.1). Sager Creek directly receives effluent discharge from Siloam Springs and is a tributary to Flint Creek. Flint Creek and the Illinois River are potentially subject to the Scenic River TP criterion at the Arkansas and Oklahoma state line. All these selected streams have some similar physical characteristics such as a
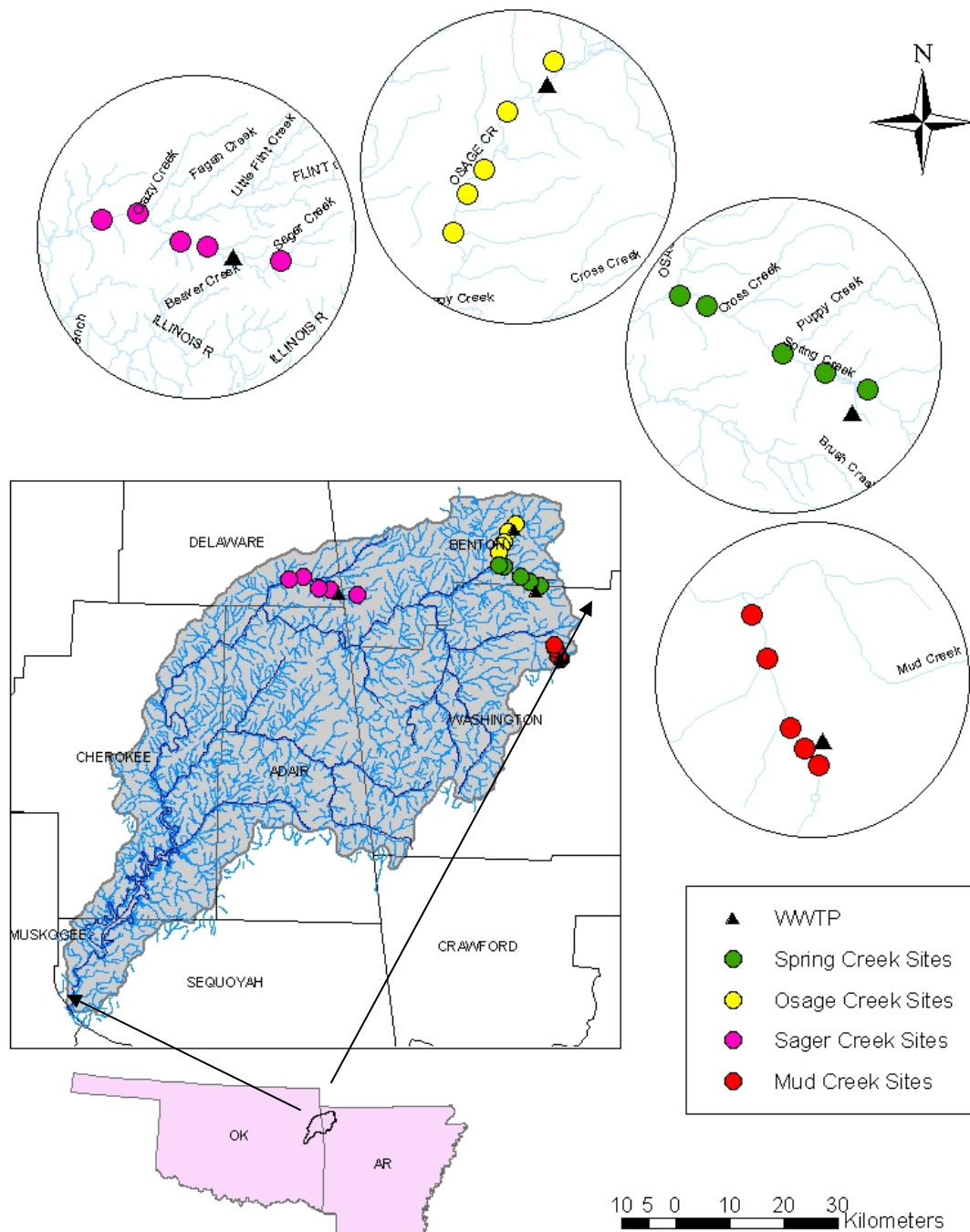
**Figure 3.1.** Water quality and sediment sampling sites upstream and downstream of municipal wastewater treatment plants at headwaters at Mud Creek, Spring Creek, Osage Creek, and Sager/Flint Creeks within the Illinois River Basin.
typical riffle-pool geomorphology with bedrock outcroppings and larger cobbles common at few sites.

At Mud Creek, I selected a site about 0.5 km upstream and downstream sites from 0.4, to 3.1 km from the WWTP input. This WWTP is at a distance of about 53 km upstream from the Arkansas-Oklahoma state border, as estimated by ArcGIS8 software (ESRI, 2003). The generic land use along the stream reach is mostly urban and almost all sampling sites are located in small urban neighborhoods within the city of Fayetteville. Fayetteville's WWTP is a tertiary level treatment plant and has current treatment capacity of about 67,000 human equivalents on a 378.5-L (100 gallons) per person per day basis. The current population of the City of Fayetteville is about 58,000. The facility has a regulatory P (1.0 mg $L^{-1}$) and N ($NH_4$: summer=2.0 mg $L^{-1}$ and winter=5.0 mg $L^{-1}$) management plan (Personal Communication with Thom Vinson, September 10, 2003). He also indicated that the annual average P concentration (July 2002 to June 2003) in effluent from this facility was about 0.25 mg $L^{-1}$.

At Spring Creek, the upstream site was about 1.1 km from WWTP input and the four downstream sites were approximately 2.0 to 7.5 km from the WWTP input. The Springdale municipal WWTP input is almost 45 km upstream from the Arkansas-Oklahoma state border, as estimated by ArcGIS8 software (ESRI, 2003). The generic land use along the selected stream reach at Spring Creek is mostly pastureland with some suburban neighborhoods surrounding the upstream and the site immediately downstream of WWTP input. The Springdale WWTP facility is an advanced secondary system with treatment capacity for about 120,881 (total suspended solids, TSS) and 167,830 people (biochemical oxygen demand, BOD). The current population of the city is approximately 45,000. The facility has limits on ammonium ($NH_4$) of 1.5 mg $L^{-1}$ monthly average in summer and 4.0 mg $L^{-1}$ monthly average in winter in the effluent, but does not have a regulatory limit on P (Personal Communication with Jennifer Enos, Lab Director, Springdale WWTP, July 8 and September 11, 2003). However, the WWTP has been making voluntary efforts to keep effluent TP concentrations < 1.0 mg $L^{-1}$. The lab director also provided data for P concentration in effluent, which indicated that the annual average P concentration (July 2002 to June 2003) in effluent from this facility was about 4.4 mg $L^{-1}$.

The selected sampling reach at Osage Creek was about 5.7 km long with an upstream site about 0.2 km from the WWTP input and the downstream sites were approximately 1.5 to 5.5 km from WWTP input. The WWTP input from City of Rogers municipal WWTP is almost 43 km upstream from the Arkansas-Oklahoma state borders. The generic land use along this stream reach is mostly pastureland and the site immediately downstream of WWTP input is within the premises of the facility. The City of Rogers facility is an advanced secondary WWTP with treatment capacity for about 35,428 human equivalents and current city population is approximately 39,000. The WWTP has a voluntary limit for P (1.0 mg $L^{-1}$) and regulatory limits for N ($NO_3$= 3 mg $L^{-1}$, $NH_4$= 1.5 mg $L^{-1}$ in summer and 2.3 mg $L^{-1}$ in winter) in the effluent (personal communication with Robert Moore, City of Rogers municipal WWTP, September 10, 2003). The annual average P concentration (July 2002 to June 2003) in effluent from this facility was about 0.35 mg $L^{-1}$ (Courtesy: Mike Lawrence, City of Rogers Municipal WWTP, July 18, 2003).

Siloam Springs WWTP is a tertiary level facility and discharges effluent into Sager Creek, a Flint Creek tributary. The selection of sites at Sager/Flint Creeks was based on easy access and interest in sampling Flint Creek. The site upstream of the WWTP input was about 3.3 km and sites downstream from the WWTP input were from 2.0 to 10.0 km. The WWTP input from Siloam Springs is very near to the Arkansas-Oklahoma state line (0.5 km) as compared to the other three municipal WWTPs. The generic land use along upstream part of this stream reach is urban and sites downstream are mostly pastureland. The current treatment capacity of this facility is about 17,000 people and city population is approximately 10,000. The facility has N management plan but no limits on P in the effluent (Personal Communication with Tom Myers, Siloam Springs WWTP, July 8, 2003). The annual average P concentration in effluent from this facility was unavailable.

The distance of water quality sampling stations downstream of the WWTP input was estimated at each stream reach (Table 3.1). The approximate distance (river km) between the sampling stations and WWTP was estimated by plotting the latitude and longitudes (GPS-V, Garmin) in ArcGIS 8 software (ESRI, 2003) and using the distance-measuring tool.

**Table 3.1.** Distance of sampling sites upstream and downstream from the municipal wastewater treatment plant (WWTP) input as estimated by ArcGIS 8 software.

| Sampling Site | Distance from the Wastewater treatment Plant Input (km) | | | |
| --- | --- | --- | --- | --- |
| | Mud Creek | Spring Creek | Osage Creek | Sager/Flint Creek |
| Upstream | -0.5 | -1.1 | -0.2 | -3.3 |
| WWTP Input | 0.0 | 0.0 | 0.0 | 0.0 |
| 1st downstream | 0.4 | 2.0 | 1.5 | 2.0 |
| 2nd downstream | 0.9 | 3.9 | 3.4 | 3.9 |
| 3rd downstream | 2.2 | 4.6 | 4.2 | 7.5 |
| 4th downstream | 3.1 | 7.5 | 5.5 | 10.0 |
| Total length | 3.6 | 8.6 | 5.7 | 13.3 |

Negative distances denote the site upstream from the municipal WWTP.

**Water Quality Sampling**

Field Techniques and Laboratory Analysis

Water samples were collected from the four headwater streams from July 2002 through June 2003 at least once a month under baseflow conditions. One reference (or background) site upstream from the WWTP and four sites downstream from the WWTP effluent were selected at each stream. Water samples were collected in two 20-ml scintillation vials (filtered with 0.45-μm nylon membranes) from the middle of the stream channel. The bottles and syringes were pre-rinsed with ambient stream water prior to collecting water samples at each site. Each of the 20-ml vials was acidified to pH < 2 with concentrated HCl at each site. All of the water quality samples collected were stored on ice and kept in dark until return to the laboratory.

Physico-chemical parameters were measured at a single point (mid-stream) at each sampling site. These measurements included specific conductivity, temperature (Orion conductivity Meter 115A plus, Beverly, MA), dissolved oxygen (YSI-Model 85, Yellow Springs, OH) and pH (pH Testr 2 double junction pH meter, Oakton Instruments, West Caldwell, NJ). Discharge was estimated at all sampling sites at a transect perpendicular to stream flow (Gore, 1996). Typically, the transect was divided in equally spaced intervals and water velocity was measured with an electromagnetic flow meter (Flo-Mate 2000; Marsh-McBirney Inc., Frederick, MD). The depth at mid-points of these width intervals was measured to obtain the cross-sectional area of stream. The discharge was estimated as a product of water velocity and cross-sectional area.

In some streams, dissolved inorganic P concentration has been shown to be approximately 75% to 95% of the amount of TP in the water column (Reddy et al., 1996; Jarvie et al., 2002) and was useful as a surrogate for evaluating changes in stream P under high P loading conditions (Dodds, 2003) such as from the WWTPs. Therefore, the filtered and acidified water samples were analyzed for soluble reactive P (SRP) colorimetrically by the ascorbic acid reduction method (APHA, 1992). The filtered and unacidified samples were analyzed with mercuric thiocyanate reaction for $Cl^-$ (Skalar Methods, the Netherlands).

Net- uptake lengths ($S_{net}$)

When evaluating changes in P concentrations and P retention, selection of a conservative solute is critical especially in stream systems where downstream dilution may occur because of groundwater contributions and other factors (Bencala et al., 1987). Chloride ($Cl^-$), a conservative solute, is widely used as a hydrologic tracer for dilution correction, especially in stream systems to observe the gradual downstream declines in P concentrations (e.g., see Marti and Sabater, 1996; Marti et al., 2003). Marti et al. (2003) used longitudinal variation of nutrient concentrations relative to $Cl^-$ concentrations downstream from several WWTP input to measure stream P retention (see also Haggard et al., 2004).

As P travels downstream, several abiotic and biotic factors may retain or transform P from the dissolved form to the particulate form. Phosphorus uptake length ($S_w$) is the distance a P molecule travels downstream in the dissolved inorganic form before uptake by biotic or abiotic processes (Newbold et al., 1981; Stream Solute Workshop 1990). In the present study, a different parameter $S_{net}$ (whole reach net uptake length, Haggard et al., 2001a) was estimated whenever a gradual decline in SRP concentrations was observed longitudinally downstream of WWTP input. The SRP concentrations at sites downstream from the WWTP input were background corrected using upstream SRP concentrations.

Dilution correction using $Cl^-$ concentrations with respect to the first site downstream from the WWTP input was also done to estimate the proportion of SRP remaining in the water column. It can mathematically be represented as:

$$C_x = C_o e^{-kx} \qquad\qquad (3.1)$$
$$\ln(C_x/C_o) = -kx \qquad\qquad (3.2)$$

where $C_x$ is the background and dilution-corrected SRP concentration (mg L$^{-1}$) at distance x (km) downstream from the WWTP effluent, $C_o$ is the corrected SRP concentration (mg L$^{-1}$) at first downstream site from WWTP effluent, and k is the SRP change coefficient (km$^{-1}$). $S_{net}$ is the inverse of the slope of the regression line relating natural logarithm of proportion of dilution-corrected SRP concentrations in the water column and downstream distance from the WWTP input (equation 3.2).

$$S_{net} = 1/slope = -1/k \quad (3.3)$$

Dilution-corrections were not used where Cl$^-$ concentrations did not change appreciably downstream of the WWTP input and only background (upstream) corrected SRP concentrations were used to estimate $S_{net}$. $S_{net}$ is used as a measure of net retention efficiency with shorter $S_{net}$ suggesting higher P retention efficiency. The distance of water quality sampling stations downstream of the WWTP input was determined to estimate $S_{net}$ at each stream reach (Table 3.1).

**Sediment Sampling**
Field Techniques

A single sediment sample was collected seasonally beginning summer 2002 through summer 2003 (July 2002, October 2002, January 2003, April 2003, June 2003) at the reference site upstream and three downstream sites of the WWTPs at all four study reaches. For sediment samplings, I left out the site before last downstream sampling site where water quality samples were collected, at each stream. Composite benthic sediments were collected with a trowel at various points along a transect perpendicular to streamflow from top 2 to 5 cm of streambed. The sediment samples were placed in plastic bags and stored in the dark until transported to the laboratory. About 1-L of stream water was collected in HDPE bottles, and stored in ice in the dark until return to the laboratory.

Laboratory Techniques and Analysis

After returning to the laboratory, sediments were sieved through a 4.5-mm sieve and particles < 4.5 mm in diameter were used in extraction procedures. Fresh, wet sediments were used to determine loosely exchangeable phosphorus (EXP), phosphorus sorption index (PSI), and equilibrium phosphorus concentration (EPC$_0$). The stream water was filtered through nylon membranes (0.45-µm pore size) to be used in extractions.

Exchangeable P (EXP) (Ruttenberg, 1992) was determined from a single extraction with 1M MgCl$_2$ and represented easily and readily exchangeable P in the benthic sediments. One hundred milliliters of 1M MgCl$_2$ was added to 20 to 30 g of fresh sediments in 250-ml Erlenmeyer flasks. The flasks were shaken in a reciprocating shaker for 1 h to mix the contents, which were also stirred vigorously for about 5 s at 15-min intervals. After 1 h, sediments in flasks were allowed to settle for about 30-min, and 15 to 20 ml of the solution was filtered through 0.45-µm nylon membranes to pre-labeled 20-ml scintillation vials. The aliquots were acidified to pH < 2 and stored in a refrigerator until analyzed for SRP. The remaining sediments were transferred to aluminum pans and dried for 48 h at 80°C to determine sediment dry mass. Exchangeable P content was determined as the amount of P extracted per unit dry weight of sediment (µg-P g$^{-1}$ dry sediment).

The P sorption index (PSI) (Klotz, 1988; Bache and Williams, 1971) is a simple single-point method for estimating sediments ability to adsorb $PO_4$-P molecules from aqueous solutions. One hundred milliliters of filtered stream water was spiked with an additional 2 mg $L^{-1}$ $PO_4$-P and added to about 20 to 30 g of fresh sediments in 250-ml Erlenmeyer flasks. The flasks were shaken in a reciprocating shaker for 1 h to mix the contents, which were stirred vigorously for about 5 s at 15-min intervals. After 1 h, sediments in flasks were allowed to settle for about 30-min, and 15 to 20 ml of the solution was filtered through 0.45-μm nylon membranes to pre-labeled 20-ml scintillation vials. The aliquots were acidified to pH < 2 and stored in a refrigerator until analyzed as previously described. The remaining sediment slurry was transferred to aluminum pans and dried for 48 h at 80°C to determine sediment dry mass. The sorption index (PSI) was calculated as:

$$PSI = \frac{X}{\log C} \tag{3.4}$$

where X is the P adsorbed by the sediments from aqueous solution (mg-P $g^{-1}$ dry sediment) and C is the final SRP concentration (mg-P $L^{-1}$) in aqueous solution after 1 h.

Equilibrium P concentration ($EPC_0$) (Froelich, 1988; Klotz, 1985) is the concentration when sediments and water column are in equilibrium and there is no net adsorption or release of $PO_4$-P from sediments to the water column (Taylor and Kunishi, 1971). Fresh, wet sediments were used for measuring $EPC_0$ since dried sediments may yield significantly higher concentrations (Klotz, 1988). Extractions for $EPC_0$ used a series of filtered stream water solutions spiked with additional P from 0.0 to 4.0 mg-P $L^{-1}$ (0.0, 0.10, 0.25, 0.50, and 2.0 mg-P $L^{-1}$ for Mud and Osage Creeks; 0.0, 0.50, 1.0, 2.0, and 4.0 mg-P $L^{-1}$ for Spring and Sager and Flint Creeks, respectively). For example, if the filtered stream water in Mud Creek had an ambient SRP concentration of 0.10 mg-P $L^{-1}$, then the series of spikes in filtered stream water initially contained becomes 0.10, 0.20, 0.35, 0.60, and 2.10 mg-P $L^{-1}$. About 20 to 30 g of fresh, wet sediments and 100-ml of filtered stream water spiked with additional $PO_4$ was added in 250-ml Erlenmeyer flasks. The flasks were sealed with a rubber stopper and kept in a reciprocating shaker for about 1 h with vigorous manual stirring for about 5 s at 15-min intervals. After 1 h, sediments in flasks were allowed to settle for about 30-min, and 15 to 20 ml of the solution was filtered through 0.45-μm nylon membranes to pre-labeled 20-ml scintillation vials. The aliquots were acidified to pH < 2 and stored in refrigerator until analyzed. The remaining sediments were transferred to aluminum pans and dried for 48 h at 80°C to determine sediment dry mass. Simple linear regression of P sorbed (μg $g^{-1}$ dry sediment) against initial SRP concentration in the solution was used to determine the $EPC_0$, which is the x-intercept (Figure 3.2).
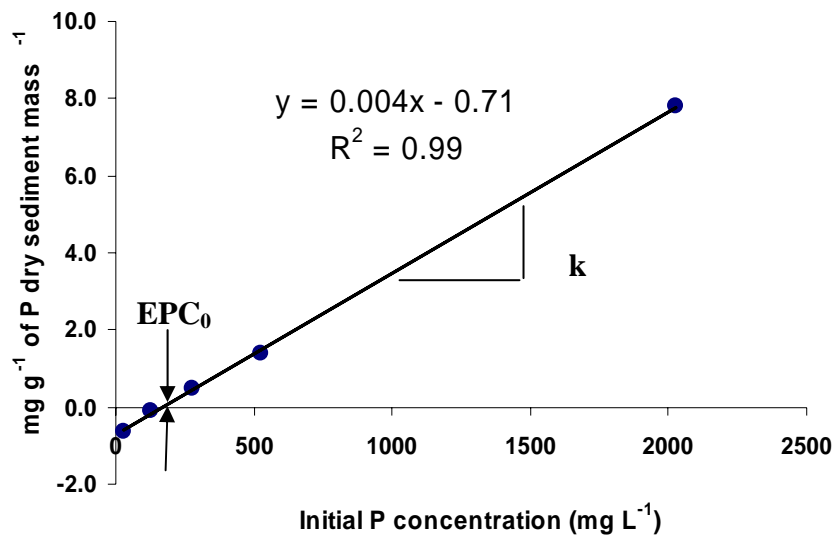
**Figure 3.2.** Simple linear regression of P sorbed (µg $g^{-1}$ dry sediment) against initial SRP concentration (mg $L^{-1}$) in the solution to calculate the sediment equilibrium P concentration ($EPC_0$).

The slope (k) of the relation between P sorbed and initial $PO_4$-P concentration represents the quantity of $PO_4$ sorbed on sediments at equilibrium. This mass may be available for release from sediments to $PO_4$ deficient solutions. This slope was used as another measure of sediment-P buffering capacity.

**Statistical Analysis**

Logarithmic transformations of the water quality data were used to achieve normality requirements (Sawyer et al., 2003). Simple linear regression was used to estimate the correlation between various parameters such as SRP and $EPC_0$, EXP and $EPC_0$ along the reach length at individual streams and combined at all streams. One-tailed paired t-test was used to determine differences between the sites upstream and immediately downstream of the WWTP input different parameters (EXP, PSI, SRP, $Cl^-$), as well as for comparisons at each site (e.g., SRP and $EPC_0$). A significance level of 0.10 was used for all comparisons and confidence interval of 90% for all regression analyses.

# RESULTS AND DISCUSSION

The first objective of this study was to compare the soluble reactive phosphorus (SRP) concentrations between the reference (upstream) and downstream sites of the WWTP input. It was hypothesized that the wastewater treatment plant (WWTP) inputs to these streams has elevated SRP concentrations in the water column. Transport, retention, and accumulation of P in streams are not only dependent on ambient P concentrations in water, but various other factors such as contribution of WWTP effluent discharge to physico-chemical properties (stream flow, conductivity, dissolved oxygen, temperature, and pH). Chloride (Cl⁻) concentrations were also measured in the water quality samples to accomplish the second objective, and are discussed later in the chapter. However, some general discussion on patterns of Cl⁻ concentrations, an important chemical constituent used as a hydrologic tracer, is included in this section as well.

Stream flow
Generally, stream flow measured at the sampling sites upstream of WWTP was much less than at sites downstream of the WWTP input. Thus, municipal WWTP effluent represented a significant part of stream flow downstream from the input across all streams (Table 4.1). Stream flow was relatively high at the site upstream from the WWTP at Osage Creek ($286 \text{ L s}^{-1}$) as compared to other streams. Streamflow downstream from the WWTP effluent discharge at Mud Creek, Spring Creek, Osage Creek, and Sager/Flint

**Table 4.1.** Stream flow (mean ± standard deviation) at each sampling site at all four study streams (Mud Creek, Spring Creek, Osage Creek, and Sager/Flint Creeks).

| Sampling Site | Average Streamflow (L/s) | | | |
| --- | --- | --- | --- | --- |
| | Mud Creek | Spring Creek | Osage Creek | Sager/Flint Creeks |
| Upstream | 3 ± 4 | 14 ± 16 | 286 ± 131 | 42 ± 26 |
| 1ˢᵗ downstream | 172 ± 127 | 698 ± 267 | 605 ± 185 | 275 ± 117 |
| 2ⁿᵈ downstream | 181 ± 125 | 601 ± 254 | 650 ± 156 | 265 ± 134 |
| 3ʳᵈ downstream | 190 ± 109 | 761 ± 299 | 625 ± 167 | 772 ± 354 |
| 4ᵗʰ downstream | 209 ± 115 | 753 ± 307 | 630 ± 169 | 893 ± 452 |

Creeks increased by an average of 57x, 50x, 2x, and 7x, respectively. The greatest increase in streamflow at sites immediately downstream from the WWTP input was observed at Mud Creek where average stream flow increased from 3 L s$^{-1}$ to 172 L s$^{-1}$. Streamflow at Sager/Flint Creeks increased sharply from 265 L s$^{-1}$ at Sager Creek to 772 L s$^{-1}$ at the first site at Flint Creek downstream from confluence of Sager and Flint Creeks. Hence, this substantial increase in stream flow (225%) between the study reach from the site 3.9 km downstream from the WWTP to the most downstream site (10 km) can be mostly attributed to the inflow from Flint Creek. The percentage increase in streamflow from the site downstream from the WWTP to the most downstream sites was only 22%, 8%, and 4% in Mud, Spring, and Osage Creeks, respectively, much less than that observed in Sager/Flint Creeks. A continuous increase in streamflow several km downstream suggests that these Ozark streams behave as gaining streams, although at some streams (other than Sager/Flint Creeks) the increase was relatively small.

Physico-chemical properties

Effluents from WWTP input had a substantial effect on the physico-chemical parameters across all streams (Tables 4.2 to 4.6). In general, conductivity, temperature, soluble reactive P (SRP) and chloride (Cl$^-$) concentrations increased at sites immediately downstream of the WWTP outfalls compared to the upstream (reference) site. However, pH and dissolved oxygen (DO) decreased downstream from the WWTP input compared to the background conditions.

**Table 4.2.** Descriptive statistics for SRP concentrations, $Cl^-$ concentrations, Conductivity, Dissolved oxygen, Temperature, and pH measured at Mud Creek.

| Parameter | Site | n | Mean | SD | Median | Minimum | Maximum |
|---|---|---|---|---|---|---|---|
| | | | | | Descriptive Statistics | | |
| SRP (mg $L^{-1}$) | Upstream | 21 | 0.02 | 0.01 | 0.03 | 0.00 | 0.16 |
| | 1-downstream | 20 | 0.11 | 0.09 | 0.09 | 0.04 | 0.42 |
| | 2-downstream | 21 | 0.10 | 0.08 | 0.05 | 0.02 | 0.24 |
| | 3-downstream | 21 | 0.10 | 0.07 | 0.09 | 0.02 | 0.40 |
| | 4-downstream | 21 | 0.09 | 0.09 | 0.05 | 0.02 | 0.23 |
| | | | | | | | |
| Chloride (mg $L^{-1}$) | Upstream | 20 | 9 | 5 | 7 | 4 | 22 |
| | 1-downstream | 20 | 43 | 48 | 18 | 8 | 64 |
| | 2-downstream | 21 | 44 | 46 | 16 | 9 | 66 |
| | 3-downstream | 21 | 47 | 49 | 20 | 3 | 90 |
| | 4-downstream | 19 | 43 | 44 | 18 | 14 | 93 |
| | | | | | | | |
| Conductivity | Upstream | 21 | 205 | 217 | 52 | 126 | 294 |
| ($\mu$S $cm^{-1}$) | 1-downstream | 21 | 586 | 607 | 150 | 283 | 909 |
| | 2-downstream | 21 | 597 | 604 | 136 | 290 | 911 |
| | 3-downstream | 21 | 580 | 591 | 139 | 270 | 911 |
| | 4-downstream | 21 | 566 | 562 | 144 | 269 | 913 |
| | | | | | | | |
| Dissolved Oxygen | Upstream | 19 | 7.7 | 7.4 | 3.1 | 2.4 | 14.8 |
| (mg $L^{-1}$) | 1-downstream | 19 | 7.7 | 7.0 | 1.9 | 3.0 | 10.8 |
| | 2-downstream | 19 | 8.2 | 7.5 | 2.1 | 3.9 | 12.3 |
| | 3-downstream | 19 | 8.1 | 7.6 | 2.4 | 2.5 | 12.4 |
| | 4-downstream | 19 | 8.5 | 7.8 | 2.6 | 2.3 | 13.2 |
| | | | | | | | |
| Temperature (°C) | Upstream | 20 | 14.3 | 16.0 | 7.0 | 4.0 | 23.8 |
| | 1-downstream | 20 | 18.1 | 17.0 | 5.4 | 10.0 | 26.9 |
| | 2-downstream | 20 | 18.1 | 16.9 | 5.3 | 10.6 | 26.8 |
| | 3-downstream | 20 | 17.2 | 17.6 | 5.4 | 9.5 | 26.1 |
| | 4-downstream | 20 | 17.0 | 17.9 | 5.6 | 8.7 | 25.6 |
| | | | | | | | |
| pH | Upstream | 20 | 7.9 | 8.1 | 0.4 | 6.6 | 8.4 |
| | 1-downstream | 20 | 7.8 | 7.8 | 0.2 | 7.4 | 8.1 |
| | 2-downstream | 20 | 8.0 | 8.0 | 0.2 | 7.6 | 8.5 |
| | 3-downstream | 20 | 8.1 | 8.0 | 0.3 | 7.6 | 8.7 |
| | 4-downstream | 20 | 8.2 | 8.1 | 0.3 | 7.7 | 9.0 |

**Table 4.3.** Descriptive statistics for SRP concentrations, Cl⁻ concentrations, Conductivity, Dissolved oxygen, Temperature, and pH measured at Spring Creek.

| Parameter | Site | n | Mean | SD | Median | Minimum | Maximum |
|---|---|---|---|---|---|---|---|
| SRP (mg $L^{-1}$) | Upstream | 20 | 0.08 | 0.08 | 0.06 | 0.03 | 0.41 |
| | 1-downstream | 21 | 2.10 | 2.24 | 1.36 | 0.13 | 7.60 |
| | 2-downstream | 21 | 1.93 | 1.86 | 0.83 | 0.25 | 6.05 |
| | 3-downstream | 21 | 1.66 | 1.45 | 0.95 | 0.27 | 5.09 |
| | 4-downstream | 21 | 1.58 | 1.16 | 1.19 | 0.20 | 3.80 |
| Chloride (mg $L^{-1}$) | Upstream | 21 | 12 | 6 | 11 | 7 | 30 |
| | 1-downstream | 21 | 63 | 15 | 62 | 41 | 89 |
| | 2-downstream | 21 | 51 | 12 | 53 | 29 | 71 |
| | 3-downstream | 21 | 46 | 12 | 46 | 24 | 72 |
| | 4-downstream | 20 | 43 | 11 | 41 | 22 | 66 |
| Conductivity ($\mu$S cm$^{-1}$) | Upstream | 21 | 278 | 55 | 273 | 191 | 365 |
| | 1-downstream | 21 | 567 | 97 | 549 | 402 | 726 |
| | 2-downstream | 21 | 532 | 90 | 526 | 370 | 721 |
| | 3-downstream | 21 | 496 | 84 | 487 | 339 | 671 |
| | 4-downstream | 21 | 470 | 92 | 472 | 294 | 661 |
| Dissolved Oxygen (mg $L^{-1}$) | Upstream | 19 | 8.4 | 3.5 | 8.0 | 1.7 | 14.0 |
| | 1-downstream | 19 | 8.2 | 2.1 | 8.4 | 1.9 | 12.3 |
| | 2-downstream | 19 | 8.6 | 2.3 | 8.8 | 1.9 | 12.8 |
| | 3-downstream | 18 | 9.7 | 2.3 | 9.3 | 5.6 | 14.3 |
| | 4-downstream | 18 | 9.6 | 2.3 | 9.0 | 5.8 | 13.7 |
| Temperature (°C) | Upstream | 21 | 15.1 | 6.4 | 16.7 | 2.8 | 25.0 |
| | 1-downstream | 21 | 18.5 | 5.3 | 19.9 | 10.4 | 26.3 |
| | 2-downstream | 21 | 18.0 | 5.4 | 19.3 | 9.7 | 26.2 |
| | 3-downstream | 21 | 17.2 | 6.1 | 18.5 | 7.3 | 26.1 |
| | 4-downstream | 21 | 17.1 | 6.3 | 18.8 | 6.8 | 25.5 |
| pH | Upstream | 20 | 7.9 | 0.4 | 7.9 | 7.4 | 8.9 |
| | 1-downstream | 20 | 7.6 | 0.2 | 7.7 | 7.1 | 7.9 |
| | 2-downstream | 20 | 7.8 | 0.2 | 7.8 | 7.4 | 8.2 |
| | 3-downstream | 20 | 8.2 | 0.2 | 8.2 | 7.7 | 8.5 |
| | 4-downstream | 20 | 8.3 | 0.3 | 8.2 | 7.8 | 8.9 |

**Table 4.4.** Descriptive statistics for SRP concentrations, Cl⁻ concentrations, Conductivity, Dissolved oxygen, Temperature, and pH measured at Osage Creek.

| Parameter | Site | n | Mean | SD | Median | Minimum | Maximum |
|---|---|---|---|---|---|---|---|
| SRP (mg $L^{-1}$) | Upstream | 21 | 0.03 | 0.03 | 0.02 | 0.01 | 0.12 |
| | 1-downstream | 21 | 0.08 | 0.07 | 0.07 | 0.02 | 0.27 |
| | 2-downstream | 21 | 0.07 | 0.04 | 0.06 | 0.02 | 0.16 |
| | 3-downstream | 21 | 0.07 | 0.04 | 0.06 | 0.02 | 0.16 |
| | 4-downstream | 21 | 0.07 | 0.03 | 0.07 | 0.03 | 0.12 |
| | | | | | | | |
| Chloride (mg $L^{-1}$) | Upstream | 20 | 10 | 8 | 7 | 4 | 37 |
| | 1-downstream | 20 | 32 | 10 | 31 | 15 | 49 |
| | 2-downstream | 21 | 31 | 9 | 30 | 13 | 45 |
| | 3-downstream | 21 | 31 | 8 | 30 | 17 | 45 |
| | 4-downstream | 21 | 30 | 8 | 30 | 17 | 45 |
| | | | | | | | |
| Conductivity ($\mu$S cm$^{-1}$) | Upstream | 21 | 275 | 38 | 264 | 212 | 337 |
| | 1-downstream | 21 | 405 | 62 | 412 | 318 | 560 |
| | 2-downstream | 21 | 375 | 52 | 382 | 297 | 460 |
| | 3-downstream | 21 | 377 | 51 | 386 | 291 | 476 |
| | 4-downstream | 21 | 374 | 53 | 377 | 288 | 476 |
| | | | | | | | |
| Dissolved Oxygen (mg $L^{-1}$) | Upstream | 19 | 7.1 | 2.4 | 7.1 | 1.1 | 10.4 |
| | 1-downstream | 19 | 7.9 | 2.3 | 7.8 | 1.3 | 11.2 |
| | 2-downstream | 19 | 8.7 | 3.0 | 8.7 | 1.2 | 14.3 |
| | 3-downstream | 19 | 8.7 | 2.7 | 8.3 | 1.4 | 14.0 |
| | 4-downstream | 19 | 9.1 | 2.8 | 9.5 | 1.4 | 13.8 |
| | | | | | | | |
| Temperature (°C) | Upstream | 21 | 15.4 | 3.9 | 17.2 | 8.3 | 20.3 |
| | 1-downstream | 21 | 16.9 | 4.2 | 18.0 | 10.1 | 22.6 |
| | 2-downstream | 21 | 16.9 | 5.0 | 18.7 | 8.5 | 24.0 |
| | 3-downstream | 21 | 16.6 | 5.1 | 18.3 | 7.9 | 23.4 |
| | 4-downstream | 21 | 16.9 | 5.7 | 19.5 | 7.3 | 24.4 |
| | | | | | | | |
| pH | Upstream | 20 | 7.6 | 0.2 | 7.6 | 7.1 | 8.0 |
| | 1-downstream | 20 | 7.6 | 0.2 | 7.6 | 7.0 | 7.7 |
| | 2-downstream | 20 | 7.8 | 0.2 | 7.8 | 7.5 | 8.1 |
| | 3-downstream | 20 | 7.9 | 0.2 | 7.8 | 7.5 | 8.3 |
| | 4-downstream | 20 | 8.0 | 0.2 | 8.0 | 7.4 | 8.3 |

**Table 4.5.** Descriptive statistics for SRP concentrations, Cl⁻ concentrations, Conductivity, Dissolved oxygen, Temperature, and pH measured at Sager/Flint Creeks.

| Parameter | Site | n | Mean | SD | Median | Minimum | Maximum |
|---|---|---|---|---|---|---|---|
| | | | | | Descriptive Statistics | | |
| SRP (mg L$^{-1}$) | Upstream | 20 | 0.12 | 0.12 | 0.08 | 0.01 | 0.46 |
| | 1-downstream | 21 | 1.03 | 0.46 | 0.96 | 0.36 | 2.24 |
| | 2-downstream | 21 | 0.98 | 0.41 | 1.09 | 0.40 | 1.94 |
| | 3-downstream | 21 | 0.25 | 0.09 | 0.25 | 0.11 | 0.53 |
| | 4-downstream | 21 | 0.22 | 0.09 | 0.21 | 0.03 | 0.47 |
| | | | | | | | |
| Chloride (mg L$^{-1}$) | Upstream | 20 | 9 | 4 | 8 | 4 | 22 |
| | 1-downstream | 21 | 42 | 11 | 38 | 28 | 66 |
| | 2-downstream | 19 | 40 | 14 | 33 | 24 | 68 |
| | 3-downstream | 19 | 20 | 7 | 18 | 15 | 41 |
| | 4-downstream | 20 | 19 | 6 | 18 | 10 | 29 |
| | | | | | | | |
| Conductivity | Upstream | 21 | 204 | 19 | 203 | 174 | 241 |
| (μS cm$^{-1}$) | 1-downstream | 21 | 444 | 86 | 439 | 286 | 601 |
| | 2-downstream | 21 | 424 | 85 | 401 | 273 | 601 |
| | 3-downstream | 21 | 302 | 45 | 310 | 228 | 375 |
| | 4-downstream | 21 | 301 | 46 | 315 | 221 | 369 |
| | | | | | | | |
| Dissolved Oxygen | Upstream | 19 | 9.3 | 2.9 | 10.2 | 1.1 | 12.0 |
| (mg L$^{-1}$) | 1-downstream | 19 | 8.7 | 3.4 | 8.5 | 1.0 | 14.5 |
| | 2-downstream | 19 | 8.5 | 3.4 | 8.1 | 1.2 | 14.3 |
| | 3-downstream | 19 | 8.7 | 2.7 | 8.6 | 1.5 | 12.1 |
| | 4-downstream | 19 | 8.8 | 3.4 | 8.4 | 1.3 | 14.2 |
| | | | | | | | |
| Temperature (°C) | Upstream | 21 | 16.0 | 5.4 | 17.8 | 6.7 | 22.4 |
| | 1-downstream | 21 | 18.6 | 7.0 | 21.0 | 8.0 | 28.4 |
| | 2-downstream | 21 | 17.5 | 7.4 | 19.5 | 6.6 | 27.4 |
| | 3-downstream | 21 | 17.5 | 6.7 | 20.0 | 7.2 | 26.9 |
| | 4-downstream | 21 | 17.4 | 7.4 | 19.7 | 6.5 | 27.4 |
| | | | | | | | |
| pH | Upstream | 19 | 7.4 | 0.5 | 7.6 | 5.8 | 8.0 |
| | 1-downstream | 19 | 7.8 | 0.3 | 7.8 | 7.0 | 8.5 |
| | 2-downstream | 19 | 7.8 | 0.3 | 7.8 | 6.8 | 8.5 |
| | 3-downstream | 19 | 7.8 | 0.3 | 7.8 | 7.1 | 8.1 |
| | 4-downstream | 19 | 7.9 | 0.3 | 7.9 | 6.9 | 8.4 |

Conductivity downstream from the WWTP effluent discharge increased more than 2x that observed upstream at Mud Creek, Spring Creek, and Sager/Flint Creeks, but at Osage Creek the increase was less than 1.5x of upstream values. Percentage increases in conductivity due to WWTP input was 185%, 103%, 47%, and 117% at Mud Creek, Spring Creek, Osage Creek, and Sager/Flint Creeks, respectively. Conductivity generally decreased with increasing distance from the WWTP; however, elevated conductivity values did not return back to the upstream (reference) values at the most downstream site from the WWTP input. At the most downstream sampling sites at each study reach, conductivity was still greater than 1.3x that observed upstream.

WWTP effluent discharge increased temperature by an average of 3.8°C, 3.4°C, 1.5°C, and 2.6°C compared to that measured upstream at Mud Creek, Spring Creek, Osage Creek, and Sager/Flint Creeks, respectively. Temperature generally decreased with increasing distance downstream from the WWTP. Temperature was still 2.7°C, 2.0°C, 1.5°C, and 1.4°C greater on average at the most downstream site from the WWTP.

Dissolved oxygen (DO) and pH showed slight decreases at sites immediately downstream from the WWTP input when compared to that measured at the reference site. However, DO and pH increased with increasing distance from the effluent discharge, exceeding the values measured at upstream sites. Generally, DO and pH varied between 7.1 to 9.6 mg L$^{-1}$ and 7.4 to 8.3 units, respectively, indicating no potential threat to the aquatic health of these stream ecosystems.

Chloride concentrations

Municipal WWTP inputs significantly increased Cl$^-$ concentrations when compared to upstream conditions at all streams (paired t-test for ln transformed data, $p<0.01$). Cl$^-$ concentrations were always less at upstream sites at all streams, except for one sampling event at Mud Creek where Cl$^-$ exceeded that measured downstream. Average Cl$^-$ concentrations at Mud Creek increased 4.8x downstream from the effluent discharge compared to that measured upstream and showed no appreciable decrease with increasing distance from the WWTP outfall. At Osage Creek, the WWTP input increased Cl$^-$ concentrations by an average of 3.2x, and Cl$^-$ concentrations were still about 3x greater at the most downstream site from the WWTP outfall, compared to concentrations measured at the upstream site. At Spring Creek and Sager/Flint Creeks, Cl$^-$ concentrations increased by an average of 5x and 4.7x, respectively, at sites immediately downstream from the WWTP input compared to concentrations at the reference site, and Cl$^-$ concentrations were still 3.9x and 2x greater at the most downstream sites, respectively. In general, Cl$^-$ concentrations at Mud and Osage Creeks did not show an appreciable decrease with increasing distance from the effluent discharge whereas Cl$^-$ concentrations at Spring and Sager/Flint Creeks decreased with increasing distance downstream from the WWTP outfalls

**Phosphorus Concentrations**

The first objective of my study to compare the soluble reactive phosphorus (SRP) concentrations between the reference (upstream) and downstream sites of the WWTP

input was based on the hypothesis that municipal WWTP inputs have elevated SRP concentrations in the water column.

In general, SRP concentrations increased significantly (paired t-test for ln transformed data, $p<0.01$) at sites downstream from the WWTP input when compared to that measured upstream across all streams (Figure 4.1). At Mud and Osage Creeks, the increase in SRP concentrations was relatively low (about 6x and 2x on average, respectively) downstream of the WWTP input. SRP concentrations at these streams did not decline appreciably with increasing distance downstream from the WWTP inputs. The lack of change in SRP concentrations combined with minor increases in stream flow with increasing distance from the effluent discharge suggested minimal, if any, P retention was occurring at Mud and Osage Creeks.

SRP concentrations were 27x greater (on average) just downstream from the WWTP outfall compared to that measured upstream at Spring Creek. The greatest SRP concentration observed at Spring Creek downstream of the WWTP outfall was 7.60 mg $L^{-1}$ in August 2002. In March 2002, an SRP concentration of 10 mg $L^{-1}$ was observed at Spring Creek (Haggard et al., 2003). Of the sites downstream from WWTP outfall, those at Spring Creek had greater SRP concentrations, especially during the first six months of my study. SRP concentrations generally declined with increasing distance from the WWTP; this stream showed the typical exponential decline in SRP that was similar to observed by Haggard et al. (2001a).
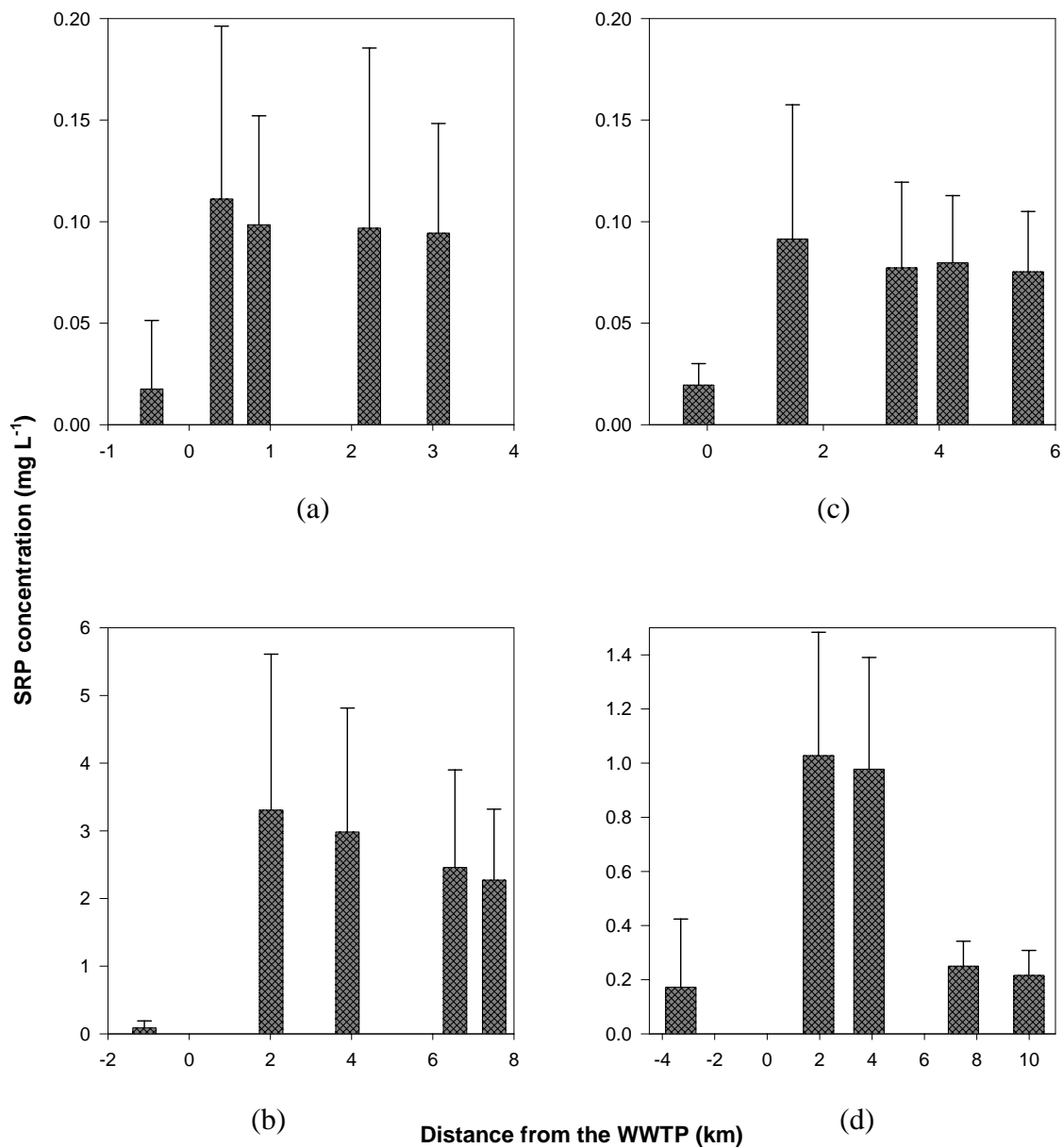
**Figure 4.1.** Changes in mean water column SRP concentrations downstream from WWTP input as a function of distance at (a) Mud Creek (b) Spring Creek (c) Osage Creek, and (d) Sager/Flint Creeks. Error bars represent the standard deviations.

SRP concentrations were 9x greater (on average) just downstream from the WWTP outfall compared to that measured upstream at Sager/Flint Creeks. The impact of the effluent discharge at this site was not as great as that observed at Spring Creek but still more profound than that observed at Mud Creek and Osage Creek. SRP concentrations at Sager/Flint Creeks decreased substantially with increasing distance from the WWTP, with the greatest decrease occurring after the confluence of Sager/Flint Creeks.

The decreasing gradient in SRP concentrations at Spring Creek and Sager/Flint Creeks may appear to suggest that P assimilation may be occurring. However, stream flow and $Cl^-$ concentrations suggested that dilution of WWTP inputs is occurring at these streams. Thus, SRP concentrations were dilution-corrected using $Cl^-$ concentrations while evaluating net retention. Therefore, my results clearly support the hypothesis that WWTP inputs elevate SRP concentrations in the water column of receiving headwater streams. Dissolved inorganic P concentrations in the WWTP effluent discharge were obtained from the municipal WWTPs for the cities of Fayetteville, Springdale, and Rogers to compare with the SRP concentrations measured during this study (July 2002 to June 2003) at the sampling sites downstream from the WWTP outfall (Figures 4.2 to 4.4). The data from the Siloam Springs WWTP effluent discharge was unavailable.
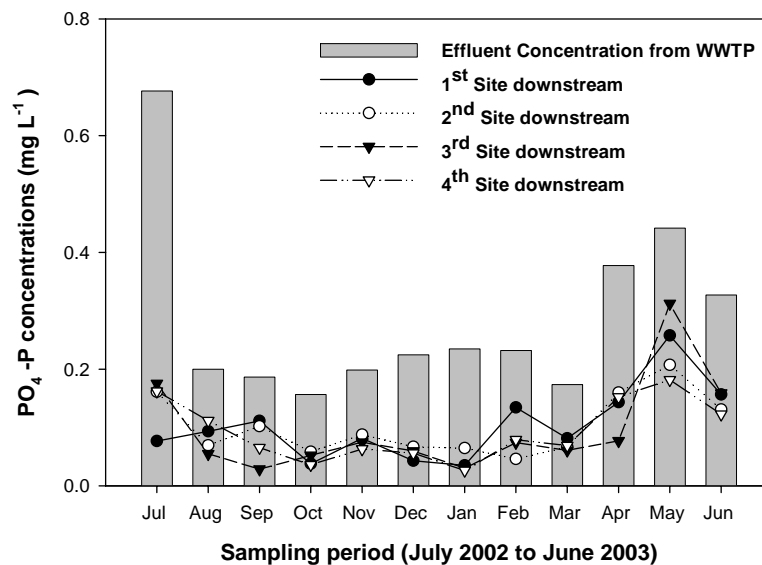


**Figure 4.2.** Comparison of $PO_4$ –P concentrations from city of Fayetteville's WWTP discharge and those measured from the water samples collected at Mud Creek.

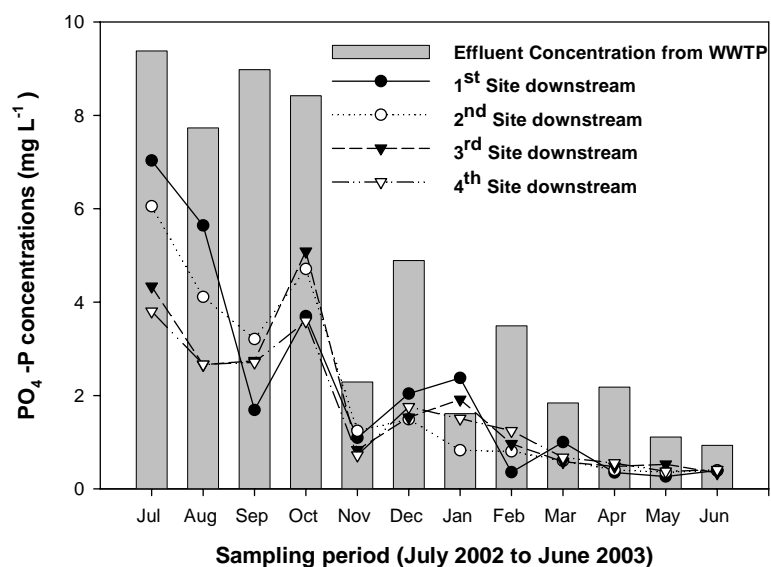**Figure 4.3.** Comparison of PO$_4$-P concentrations from Springdale WWTP discharge and those measured from the water samples collected at Spring Creek.



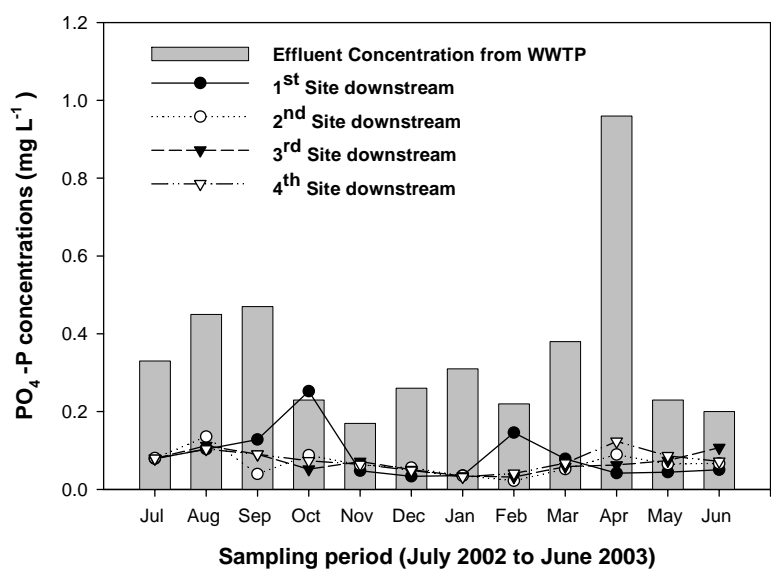**Figure 4.4.** Comparison of PO$_4$-P concentrations from Rogers WWTP and those measured from the water samples collected at Osage Creek.

SRP concentrations obtained from WWTPs and those measured at various sampling sites downstream were slightly different. This difference in dissolved P concentrations was because the data provided by the municipal WWTPs were of the actual effluent being discharged into the stream and because the effluent P was diluted by the stream it discharged into. This difference was generally magnified at sites further downstream from the effluent discharge because of additional dilution from groundwater and lateral sources, as well as the potential for P assimilation-especially under high P loading (concentration) conditions. The temporal changes in stream SRP concentration were reflected in the monthly changes in the effluent discharge. Of particular interest are dissolved P concentrations obtained from the Springdale municipal WWTP (Figure 4.3), which contributes more than 83% of P loading from WWTPs in Illinois River Basin (Haggard et al., 2003). The Springdale municipal WWTP has adjusted to P management strategies voluntarily, and this is evident in the observed P concentrations in the effluent. P concentrations measured from this study are strongly correlated to that of Springdale municipal WWTP effluent ($R^2$=0.60). The decreasing concentrations with time from WWTP and water quality samplings reflect the voluntary efforts of this WWTP to reduce P concentrations in the effluent within last year.

**Phosphorus net uptake lengths**

The second objective of my study was to examine the longitudinal variations in SRP and Cl⁻ concentrations, if any, along the stream reach. It was hypothesized that dilution and not assimilation was responsible for any variation in the SRP and Cl⁻ concentrations.

Longitudinal decline in Cl⁻ concentrations suggested that dilution from groundwater and lateral contributions was a substantial factor at Spring Creek and Sager/Flint Creeks. Therefore, Cl⁻ concentrations at these study reaches were used to make dilution-corrections in SRP concentrations to check the hypothesis that dilution was responsible for SRP concentration declines downstream, and not assimilation. Several studies have shown that Cl⁻ concentrations decreased with increasing distance from the WWTP effluent discharge (Neal et al., 1998 ; Marti et al., 2003) whereas others have shown that Cl⁻ concentrations did not show appreciable change (Haggard et al., 2001a). This suggested need to use a hydrologic tracer for dilution correction may be specific to a stream, but definitely needs to be considered when evaluating trends in constituent concentrations with increasing distance from municipal WWTPs.

Ambient SRP concentrations also decreased with distance at Spring Creek and Sager/Flint Creeks, and therefore dilution-corrections were required to estimate net P retention. Average dilution-corrected SRP values were greater than the average SRP concentrations at respective sampling stations at Spring Creek and Sager/Flint Creeks and generally increased with distance from the WWTP (Figures 4.5 and 4.6). These results indicated that dilution was likely responsible for declining SRP concentrations with increasing distance from WWTP inputs at Spring and Sager/Flint Creeks. In contrast, dilution-corrections were not necessarily needed at Mud and Osage Creeks, because Cl⁻ concentrations did not appreciably decline with increasing distance from WWTP inputs; ambient SRP concentrations did not generally decrease in the downstream direction either.

Therefore, the results support the hypothesis that dilution was responsible for declining P concentrations with increasing distance downstream from the WWTP inputs at Spring and Sager/Flint Creeks, whereas negligible retention of P was occurring at Mud Creek and Osage Creek.
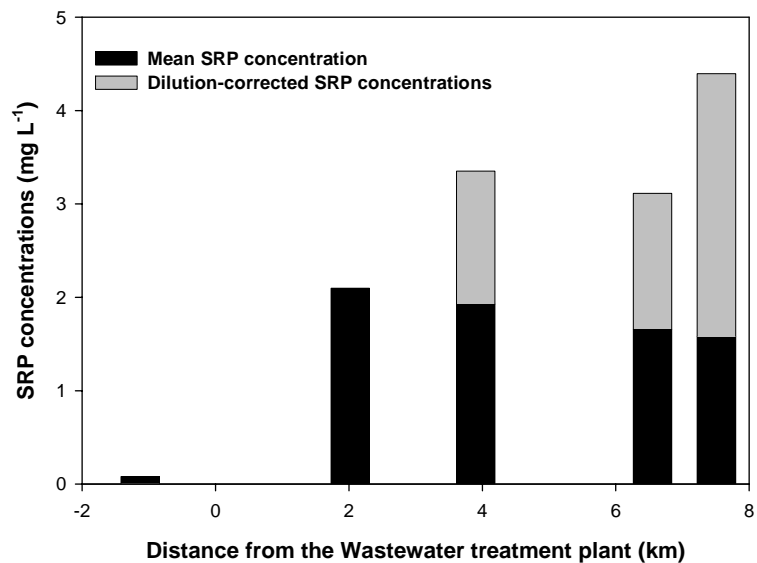


**Figure 4.5.** Comparison of mean dilution-corrected SRP concentrations with mean SRP concentrations at Spring Creek with distance downstream from the Springdale WWTP.
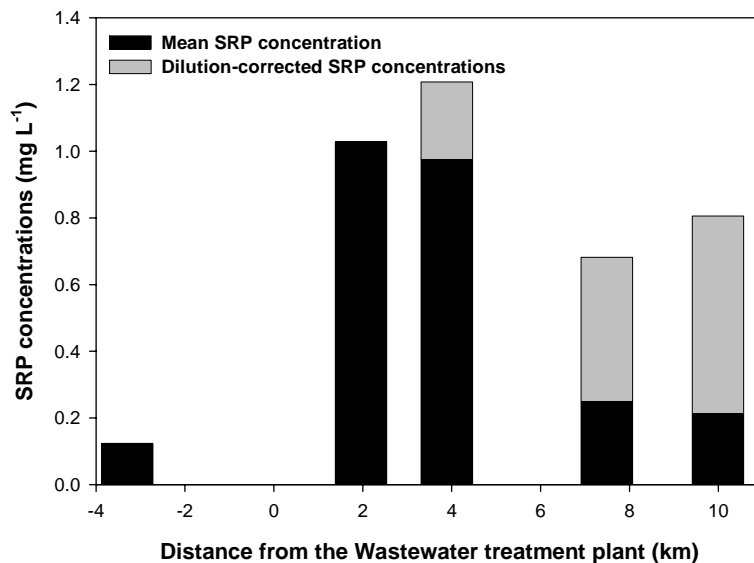


**Figure 4.6.** Comparison of mean dilution-corrected SRP concentrations with mean SRP concentrations in Sager/Flint Creeks downstream from the Siloam Springs WWTP.

To estimate net P retention efficiency ($S_{net}$) at Spring and Sager/Flint Creeks, proportion of background and dilution-corrected SRP concentrations was used. However, for Mud Creek and Osage Creek only background-corrected SRP concentrations were used to estimate $S_{net}$. In general, $S_{net}$ was not significant on many dates at the stream-reaches under study suggesting little or no P retention at these Ozark streams. Negative $S_{net}$ were significant on some dates indicating release of previously retained P in to the water column (see also Haggard et al., 2004).

Mud Creek had significant $S_{net}$ lengths on only three dates varying from -8.4 to 43 km downstream from the WWTP input (Table 4.6) whereas 18 out of 21 sampling dates showed no net P retention at Mud Creek. Similar results were observed for Osage Creek where five sampling dates had significant $S_{net}$ lengths ranging from -4.8 to 18 km downstream from the WWTP (Table 4.8). Thus, these study reaches were a sink or source of P but on most dates sampled it is clear that these streams were simply behaving as conduits for P transport where negligible P retention occurs on a net basis.

At Spring Creek, $S_{net}$ was significant on 7 out of all 21 sampling events and ranged from -18.6 to 8.2 km (Table 4.7). When $S_{net}$ lengths were significant, 6 out of 7 were negative suggesting the study reach at Spring Creek was an internal source of P. Interestingly, all negative $S_{net}$ values occurred after November 2002 when the Springdale municipal WWTP started reducing effluent P concentrations following voluntary P management. Thus, after effluent P concentration reductions, P was still not significantly retained within this system and on some occasions P previously stored within stream reach was released into the water column.

**Table 4.6.** Estimated net uptake length ($S_{net}$) at Mud Creek.

| Date | Equation | $R^2$ | p-value | Snet (km) |
|---|---|---|---|---|
| 07/15/2003 | y=0.2157x+0.226 | 0.47 | 0.31 | |
| 08/09/2002 | y=0.1463x-0.4731 | 0.17 | 0.59 | |
| 08/19/2002 | y=0.1223x-0.1607 | 0.11 | 0.66 | |
| 08/23/2002 | y=-0.0989x-0.1425 | 0.10 | 0.69 | |
| **09/14/2002** | **y=-0.7359x+0.3604** | **0.80** | **0.10** | **1. 36** |
| 09/28/2002 | y=-0.0076x-0.2701 | 0.00 | 0.98 | |
| 10/05/2002 | y=-0.0725x+0.3683 | 0.07 | 0.74 | |
| 11/17/2002 | y=-0.0153x+0.0999 | 0.01 | 0.88 | |
| 11/30/2002 | y=-0.2902x+0.2054 | 0.71 | 0.15 | |
| 12/19/2002 | y=0.0835x+0.353 | 0.08 | 0.71 | |
| **12/28/2002** | **y=0.1188x+0.0064** | **0.90** | **0.05** | **-8. 41** |
| 01/07/2003 | y=-0.1831x+0.4929 | 0.23 | 0.52 | |
| 02/03/2003 | y=0.3982x-0.9412 | 0.32 | 0.43 | |
| 02/20/03 | N.A.* | | | |
| 03/06/2003 | y=0.2742x-0.5389 | 0.20 | 0.96 | |
| 03/24/2003 | y=0.0734x-0.0465 | 0.68 | 0.17 | |
| 04/11/2003 | y=-0.0855x+0.0174 | 0.08 | 0.71 | |
| 05/08/2003 | y=0.099x-0.152 | 0.13 | 0.64 | |
| 05/29/2003 | y=0.1142x+0.3099 | 0.12 | 0.65 | |
| 06/08/2003 | y=-0.1008x-0.0683 | 0.16 | 0.61 | |
| **06/18/2003** | **y= -0.0228x+0.0016** | **0.91** | **0.04** | **43. 86** |

* N.A. indicates that no $S_{net}$ was calculated for that date.

**Table 4.7.** Estimated net uptake length ($S_{net}$) at Spring Creek.

| Date | Equation | $R^2$ | p-value | Snet (km) |
|------|----------|-------|---------|-----------|
| 07/19/2002 | y=0.0372x-0.021 | 0.22 | 0.53 | |
| 08/09/2002 | y=-0.0578x-0.3444 | 0.16 | 0.60 | |
| **08/19/2002** | **y=-0.1216x+0.2515** | **0.95** | **0.02** | **8.22** |
| 08/23/2002 | y=-0.0441x+0.1279 | 0.69 | 0.17 | |
| 09/14/2002 | y=0.1244x+0.0107 | 0.46 | 0.32 | |
| 09/28/2002 | y=0.1063x-0.0072 | 0.29 | 0.46 | |
| 10/12/2002 | y=0.0413x+0.0129 | 0.43 | 0.34 | |
| **11/17/2002** | **y=0.0536x-0.0928** | **0.95** | **0.03** | **-18.65** |
| 11/30/2002 | y=0.0114x+0.1074 | 0.04 | 0.80 | |
| 12/19/2002 | y=0.0082x-0.3121 | 0.00 | 0.95 | |
| **12/28/2002** | **y=0.063x-0.1831** | **0.85** | **0.08** | **-15.87** |
| 01/10/2003 | y=0.085x-0.2657 | 0.30 | 0.45 | |
| **02/03/2003** | **y=0.3741x-0.3603** | **0.82** | **0.09** | **-2.67** |
| **02/20/2003** | **y=0.291x-0.3724** | **0.84** | **0.08** | **-3.43** |
| 03/06/2003 | y=-0.0667x-0.3304 | 0.08 | 0.71 | |
| 03/24/2003 | y=0.0003x+0.019 | 0.00 | 0.98 | |
| **04/13/2003** | **y=0.0852x-0.1773** | **0.98** | **0.01** | **-0.08** |
| **05/08/2003** | **y=0.2445x-0.311** | **0.87** | **0.06** | **-4.08** |
| 05/29/2003 | y=0.197x-0.0684 | 0.65 | 0.19 | |
| 06/08/2003 | N. A.* | | | |
| 06/17/2003 | y=0.042x-0.1544 | 0.19 | 0.57 | |

* N.A. indicates that no $S_{net}$ was calculated for that date.

**Table 4.8.** Estimated net uptake length ($S_{net}$) at Osage Creek.

| Date | Equation | $R^2$ | p-value | Snet (km) |
|---|---|---|---|---|
| 07/24/2002 | y=0.0021x+0.002 | 0.17 | 0.59 | |
| 08/09/2002 | y=0.2317x-0.1087 | 0.64 | 0.20 | |
| 08/20/2002 | y=0.0242x+0.025 | 0.21 | 0.55 | |
| **08/23/2002** | **y=-0.2313x+0.4237** | **0.91** | **0.05** | **4.32** |
| 09/17/2002 | y=-0.0219x-0.4795 | 0.00 | 0.95 | |
| 09/28/2002 | y=-0.1791x-0.2189 | 0.18 | 0.58 | |
| 10/05/2002 | y=-0.3936x+0.3102 | 0.70 | 0.17 | |
| 11/17/2002 | y=0.1002x-0.0386 | 0.56 | 0.25 | |
| **12/03/2002** | **y=0.4306x-0.2352** | **0.86** | **0.07** | **-2.32** |
| 12/19/2002 | y=0.2297x-0.0522 | 0.54 | 0.27 | |
| **12/28/2002** | **y=0.2086x-0.2352** | **0.87** | **0.07** | **-4.79** |
| **01/09/2003** | **y=-0.0553x+0.1037** | **0.91** | **0.05** | **18.07** |
| 02/06/2003 | N.A.* | | | |
| 02/20/2003 | N.A.* | | | |
| 03/06/2003 | y=-0.1893x-0.2792 | 0.17 | 0.59 | |
| 03/25/2003 | y=0.1276x-0.1005 | 0.79 | 0.11 | |
| 04/11/2003 | y=0.2855x-0.3463 | 0.75 | 0.13 | |
| 05/08/2003 | N. A.* | | | |
| 05/29/2003 | y=0.2125x-0.5281 | 0.64 | 0.20 | |
| 06/08/2003 | y=0.335x-0.1181 | 0.34 | 0.42 | |
| **06/18/2003** | **y= 0.3052x-0.3234** | **0.90** | **0.05** | **-3. 27** |

* N.A. indicates that no $S_{net}$ was calculated for that date.

$S_{net}$ calculations at Sager/Flint Creeks somehow contrasted those estimates at the other streams. $S_{net}$ lengths were significant on 8 sampling events, ranging from 3.6 to 8.1 km (Table 4.9). These results suggest that this stream reach was not an internal P source on any sampling date in this study (no negative $S_{net}$) values. It appears that P is often significantly retained at this study reach.

The results of this study are similar to that reported in other studies evaluating net P retention or $S_{net}$ downstream from WWTP effluent discharge (Haggard et al., 2001a; 2004; Marti et al., 2003) as well as an agricultural point source (Reddy et al, 1996). Marti et al. (2003) estimated significant $S_{net}$ values for $PO_4$-P on 55% of sampling dates at streams below WWTPs outfall; thus, almost half showed no significant retention. In these Ozark streams, significant $S_{net}$ occurred only on 27% of the total sampling dates. The long $S_{net}$ values (up to 43 km) from this study suggest lower P retention efficiency of these Ozark streams, therefore, demonstrating the impact of WWTP effluent on function of these aquatic ecosystems.

**Table 4.9.** Estimated net uptake length ($S_{net}$) at Sager/Flint Creeks.

| Date | Equation | $R^2$ | p-value | Snet (km) |
|---|---|---|---|---|
| 07/24/2002 | y=-0.0763x+0.2025 | 0.56 | 0.25 | |
| 08/09/2002 | y=-0.066x+0.2725 | 0.30 | 0.45 | |
| **08/20/2002** | **y=-0.177x+0.4534** | **0.90** | **0.05** | **5.69** |
| 08/23/2002 | y=-0.1216x+0.4214 | 0.44 | 0.33 | |
| **09/14/2002** | **y=-0.2043x+0.6308** | **0.82** | **0.09** | **4.89** |
| 09/28/2002 | y=-0.3281x+2.0234 | 0.42 | 0.35 | |
| 10/12/2002 | y=-0.1139x+0.2718 | 0.25 | 0.50 | |
| **11/17/2002** | **y=-0.1674x+0.3261** | **0.96** | **0.02** | **5.98** |
| 11/30/2002 | y=-0.105x+0.0082 | 0.50 | 0.29 | |
| **12/19/2002** | **y=-0.1335x+0.2202** | **0.99** | **0.003** | **7.49** |
| 12/28/2003 | N. A.* | | | |
| 01/10/2003 | y=-0.1286x+0.2721 | 0.99 | 0.003 | |
| **02/06/2003** | **y=-0.2759x+0.4303** | **0.99** | **0.004** | **3.62** |
| 02/17/2003 | y=0.3165x-1.2042 | 0.78 | 0.11 | |
| **03/03/2003** | **y=-0.2261x+0.6794** | **0.90** | **0.05** | **4.42** |
| **03/25/2003** | **y= -0.1226x+0.2705** | **0.91** | **0.05** | **8.15** |
| 04/13/2003 | y= -0.1216x+0.1806 | 0.40 | 0.37 | |
| 05/08/2003 | N.A.* | | | |
| 05/29/2003 | y= -0.0151x-0.1689 | 0.01 | 0.88 | |
| **06/08/2003** | **y= -0.2169x+0.7108** | **0.83** | **0.08** | **4.61** |
| 06/17/2003 | y= -0.0155x+0.0283 | 0.10 | 0.68 | |

* N.A. indicates that no $S_{net}$ was calculated for that date.

**Relationship between SRP and Sediment-P properties**

The final objective of my study was to examine sediments ability to adsorb and release P by measuring different sediment-P properties such as equilibrium P concentration ($EPC_0$), exchangeable P (EXP), and P sorption index (PSI). In addition, this section also discusses the later half of my first objective to compare sediment-P properties at sites upstream and downstream of the WWTP input. This later half of the first objective is related to the hypothesis that P enrichment from WWTPs has elevated sediment-bound P in these Ozark streams, as well as water column P concentrations.

Sediment Equilibrium P Concentrations ($EPC_0$)

Similar to the water column SRP concentrations, the $EPC_0$ increased substantially at sites downstream of the WWTP input at all streams (Figure 4.7). At Mud Creek, sediment $EPC_0$ increased significantly (paired t-test for ln transformed data, p<0.01) from an average of 0.01 mg $L^{-1}$ at the reference site to 0.18 mg $L^{-1}$ at first site downstream from the WWTP outfall. Sediment $EPC_0$ downstream from the WWTP effluent discharge was relatively similar at Mud Creek study reach. At the most downstream site, sediment $EPC_0$ was still 15x greater than that measured at the upstream site (Figure 4.7a and Table 4.10). Sediment $EPC_0$ was significantly greater than the SRP concentrations (paired t-test for ln transformed data, p<0.10) at the site immediately downstream (0.5 km) from the WWTP input, suggesting that the sediments may be acting as an internal source of P. At the other sampling and sediment sampling sites, sediment $EPC_0$ was not significantly different than SRP concentrations on the sampling dates (paired t-test for ln transformed data, p>0.10). Interestingly, stream sediments and water were not in equilibrium at the

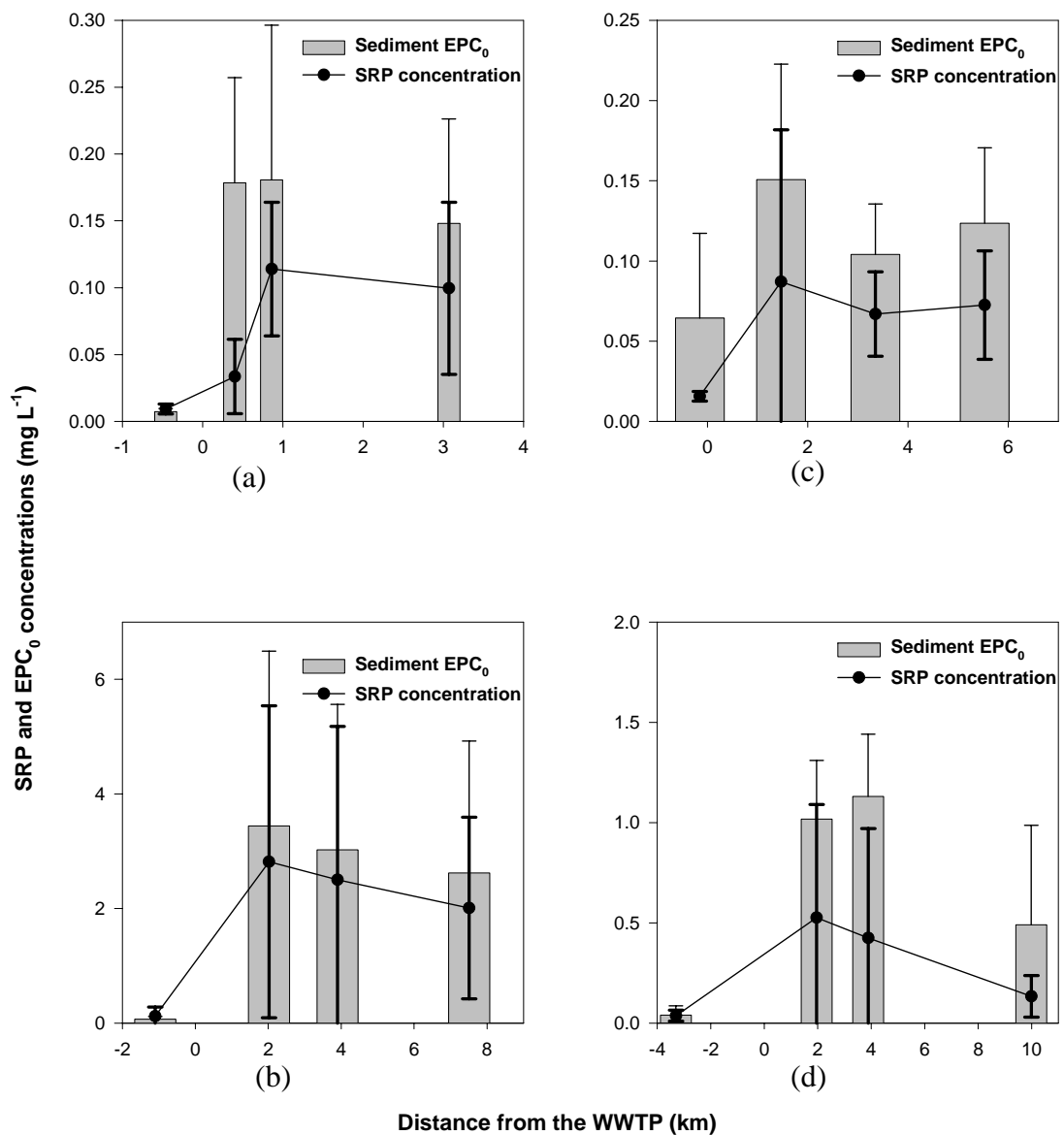**Figure 4.7.** Relationship between soluble reactive P (SRP) and equilibrium P concentrations (EPC$_0$) at: (a) Mud Creek (b) Spring Creek (c) Osage Creek, and (d) Sager/Flint Creeks. Light and dark error bars represent standard deviation of SRP concentrations and EPC$_0$ respectively.

**Table 4.10.** Simple linear regression of P sorbed by sediments as a function of initial SRP concentration during sediment $EPC_0$ extractions for Mud Creek.

| Date | $EPC_0$ mg $L^{-1}$ | Slope (k) | $R^2$ | P |
|---|---|---|---|---|
| | 0.5 km upstream of the WWTP input | | | |
| July 2002 | <0.01 | 6.08 | 0.99 | <0.01 |
| October 2002 | 0.01 | 5.00 | 0.99 | <0.01 |
| January 2003 | 0.01 | 5.94 | 0.99 | <0.01 |
| April 2003 | 0.01 | 5.24 | 0.99 | <0.01 |
| June 2003 | 0.01 | 5.40 | 0.99 | <0.01 |
| **Mean ± SD** | **0.01 ± 0.0** | **5.53 ± 0.46** | | |
| | 0.4 km downstream of the WWTP input | | | |
| July 2002 | 0.18 | 4.07 | 0.99 | <0.01 |
| October 2002 | 0.04 | 4.48 | 0.99 | <0.01 |
| January 2003 | 0.21 | 4.49 | 0.99 | <0.01 |
| April 2003 | 0.23 | 4.16 | 0.99 | <0.01 |
| June 2003 | 0.23 | 4.71 | 0.99 | <0.01 |
| **Mean ± SD** | **0.18 ± 0.08** | **4.38 ± 0.26** | | |
| | 0.9 km downstream of the WWTP input | | | |
| July 2002 | 0.06 | 5.71 | 0.99 | <0.01 |
| October 2002 | 0.05 | 5.38 | 0.99 | <0.01 |
| January 2003 | 0.29 | 4.77 | 0.99 | <0.01 |
| April 2003 | 0.25 | 4.36 | 0.99 | <0.01 |
| June 2003 | 0.26 | 4.56 | 0.99 | <0.01 |
| **Mean ± SD** | **0.18 ± 0.12** | **4.96 ± 0.57** | | |
| | 3.1 km downstream of the WWTP input | | | |
| July 2002 | 0.09 | 3.72 | 0.98 | <0.01 |
| October 2002 | 0.05 | 3.59 | 0.99 | <0.01 |
| January 2003 | 0.17 | 4.19 | 0.99 | <0.01 |
| April 2003 | 0.24 | 4.12 | 0.99 | <0.01 |
| June 2003 | 0.19 | 4.75 | 0.99 | <0.01 |
| **Mean ± SD** | **0.15 ± 0.08** | **4.07 ± 0.46** | | |

first site downstream from the WWTP but were in equilibrium at the two sites further downstream. It is possible that reduced effluent P loads resulted in SRP concentrations less than sediment $EPC_0$ 0.5 km downstream and then sediments released P until equilibrium was attained at the more downstream sites.

$EPC_0$ and SRP concentrations at Osage Creek were similar in magnitude (less than 0.20 mg $L^{-1}$) to those observed at Mud Creek (Figure 4.7c and Table 4.11); however, sediment $EPC_0$ at the Osage Creek reference site was greater than that observed at Mud Creek. But similar to Mud Creek, the effluent from the WWTP increased sediment $EPC_0$; however, the magnitude of the increase at Osage Creek was not as great as that observed at Mud Creek. Sediment $EPC_0$ increased 2.2x at the first site downstream from the WWTP compared to the reference site, and a slight decrease in sediment $EPC_0$ occurred with increasing distance from the WWTP. Sediment $EPC_0$ was still 2x greater 5.5 km downstream from the WWTP compared to background measures. Sediment $EPC_0$ was not significantly greater than SRP concentrations (paired t-test for ln transformed data, $p>0.10$) at the site immediately downstream from the WWTP outfall and the most downstream site, whereas sediment $EPC_0$ and SRP concentrations were significantly different at sampling sites upstream and at the site 4.2 km downstream from the WWTP input (paired t-test for ln transformed data, $p<0.10$). Thus, the sampling sites with sediment $EPC_0$ significantly greater than water column SRP concentration may be a potential internal source of P. It is particularly noteworthy that sediments upstream of WWTP input may be releasing P to the stream at least at the site and on the dates sampled.

**Table 4.11.** Simple linear regression of P sorbed by sediments as a function of initial SRP concentration during sediment $EPC_0$ extractions for Osage Creek.

| Date | $EPC_0$ mg $L^{-1}$ | Slope (k) | $R^2$ | P |
|---|---|---|---|---|
| | 0.2 km upstream of the WWTP input | | | |
| July 2002 | 0.02 | 6.35 | 0.99 | <0.01 |
| October 2002 | 0.03 | 5.68 | 0.99 | <0.01 |
| January 2003 | 0.15 | 5.79 | 0.99 | <0.01 |
| April 2003 | 0.04 | 5.93 | 0.99 | <0.01 |
| June 2003 | 0.07 | 5.93 | 0.99 | <0.01 |
| **Mean ± SD** | **0.06 ± 0.05** | **5.94 ± 0.26** | | |
| | 1.5 km downstream of the WWTP input | | | |
| July 2002 | 0.14 | 5.19 | 0.99 | <0.01 |
| October 2002 | 0.04 | 5.01 | 0.99 | <0.01 |
| January 2003 | 0.22 | 5.78 | 0.99 | <0.01 |
| April 2003 | 0.20 | 6.10 | 0.99 | <0.01 |
| June 2003 | 0.10 | 5.79 | 0.99 | <0.01 |
| **Mean ± SD** | **0.14 ± 0.07** | **5.58 ± 0.46** | | |
| | 3.4 km downstream of the WWTP input | | | |
| July 2002 | 0.12 | 4.70 | 0.99 | <0.01 |
| October 2002 | 0.07 | 4.99 | 0.99 | <0.01 |
| January 2003 | 0.08 | 5.78 | 0.99 | <0.01 |
| April 2003 | 0.15 | 5.71 | 0.99 | <0.01 |
| June 2003 | 0.09 | 4.96 | 0.99 | <0.01 |
| **Mean ± SD** | **0.10 ± 0.03** | **5.23 ± 0.49** | | |
| | 5.5 km downstream of the WWTP input | | | |
| July 2002 | 0.14 | 6.13 | 0.99 | <0.01 |
| October 2002 | 0.08 | 4.83 | 0.99 | <0.01 |
| January 2003 | 0.19 | 5.56 | 0.99 | <0.01 |
| April 2003 | 0.09 | 5.06 | 0.99 | <0.01 |
| June 2003 | 0.08 | 4.87 | 0.99 | <0.01 |
| **Mean ± SD** | **0.12 ± 0.05** | **5.29 ± 0.55** | | |

Sediment $EPC_0$ at Spring Creek showed greatest increase from 0.08 mg $L^{-1}$ at the upstream site to 3.38 mg $L^{-1}$ at site immediately downstream from the WWTP outfall (Figure 4.7b and Table 4.12) as compared to the other streams. Sediment $EPC_0$ decreased, similar to SRP concentrations, with increasing distance from the WWTP, but even at furthermost site 7.5 km downstream of the WWTP outfall sediment $EPC_0$ was almost 35x greater than that observed at the upstream site. At Spring Creek, sediment $EPC_0$ and water column SRP concentrations were only significantly different at the site immediately downstream from the WWTP input (paired t-test for ln transformed data, $p<0.10$). The other two sites downstream from the WWTP had marginally significant (paired t-test for ln transformed data, $p=0.11$) differences between sediment $EPC_0$ and SRP concentrations. However, at the upstream site there was no significant difference (paired t-test for ln transformed data, $p>0.10$) between $EPC_0$ and SRP concentrations.

**Table 4.12.** Simple linear regression of P sorbed by sediments as a function of initial SRP concentration during sediment $EPC_0$ extractions for Spring Creek.

| Date | $EPC_0$ mg $L^{-1}$ | Slope (k) | $R^2$ | P |
|---|---|---|---|---|
| | 1.1 km upstream of the WWTP input | | | |
| July 2002 | 0.13 | 5.85 | 0.99 | <0.01 |
| October 2002 | 0.07 | 5.43 | 0.99 | <0.01 |
| January 2003 | 0.08 | 5.20 | 0.99 | <0.01 |
| April 2003 | 0.01 | 4.63 | 0.99 | <0.01 |
| June 2003 | 0.04 | 5.64 | 0.99 | <0.01 |
| **Mean ± SD** | **0.07 ± 0.05** | **5.35 ± 0.47** | | |
| | 2.0 km downstream of the WWTP input | | | |
| July 2002 | 6.99 | 5.13 | 0.97 | <0.01 |
| October 2002 | 6.30 | 9.82 | 0.90 | 0.01 |
| January 2003 | 2.62 | 5.23 | 0.99 | <0.01 |
| April 2003 | 0.73 | 5.22 | 0.99 | <0.01 |
| June 2003 | 0.55 | 4.33 | 0.99 | <0.01 |
| **Mean ± SD** | **3.44 ± 3.05** | **5.95 ± 2.20** | | |
| | 3.9 km downstream of the WWTP input | | | |
| July 2002 | 5.19 | 5.12 | 0.96 | <0.01 |
| October 2002 | 6.08 | 9.59 | 0.99 | <0.01 |
| January 2003 | 2.59 | 4.21 | 0.94 | <0.01 |
| April 2003 | 0.71 | 4.72 | 0.99 | <0.01 |
| June 2003 | 0.55 | 4.72 | 0.99 | <0.01 |
| **Mean ± SD** | **3.03 ± 2.53** | **5.67 ± 2.22** | | |
| | 7.5 km downstream of the WWTP input | | | |
| July 2002 | 3.68 | 5.03 | 0.99 | <0.01 |
| October 2002 | 6.09 | 11.73 | 0.99 | <0.01 |
| January 2003 | 1.99 | 4.66 | 0.99 | <0.01 |
| April 2003 | 0.85 | 5.49 | 0.99 | <0.01 |
| June 2003 | 0.50 | 4.41 | 0.99 | <0.01 |
| **Mean ± SD** | **2.62 ± 2.30** | **6.26 ± 3.08** | | |

Sediment $EPC_0$ at Sager/Flint Creeks also increased from 0.05 mg $L^{-1}$ at the upstream site to 1.02 mg $L^{-1}$ downstream from the WWTP input (Figure 4.7d and Table 4.13). Sediment $EPC_0$ was still 12x greater at the most downstream site about 10 km from the WWTP input. At all sampling sites downstream from the WWTP, the sediment $EPC_0$ was significantly greater than water column SRP concentrations (paired t-test for ln transformed data, $p<0.10$). Only at the upstream site there was no significant difference between sediment $EPC_0$ and SRP concentrations (paired t-test for ln transformed data, $p<0.10$). Thus, sediments were acting as a potential source of P on these sampling dates downstream from the WWTP.

In general, increased sediment $EPC_0$ at all streams is one line of evidence supporting the hypothesis that WWTP inputs have elevated the sediment-P. Therefore, the relationship of sediment $EPC_0$ to water column SRP might be important in the mechanism of controlling or maintaining P concentrations at these streams. In this study, sediment $EPC_0$ was either in equilibrium with water column SRP concentrations or greater than SRP concentrations suggesting sediments could be a potential internal P source.

Overall, a strong correlation (simple linear regression for ln transformed data, $R^2=0.61$, $p<0.01$, ln $EPC_0=0.79$ ln SRP $+ 0.15$) existed between SRP concentrations and sediment $EPC_0$ across all streams (Figure 4.8). Therefore, the hypothesis that SRP and $EPC_0$ relationships could possibly control P concentrations in streams (see also Froelich 1988; Klotz, 1988) is verified. However, these results must be interpreted cautiously as it may be difficult to decide the regulating factor between sediment $EPC_0$ and SRP because not all the variables influencing $EPC_0$ were considered in this investigation.

**Table 4.13.** Simple linear regression of P sorbed by sediments as a function of initial SRP concentration during sediment $EPC_0$ extractions for Sager/Flint Creeks.

| Date | $EPC_0$ mg $L^{-1}$ | Slope (k) | $R^2$ | P |
|---|---|---|---|---|
| | 3.3 km upstream of the WWTP input | | | |
| July 2002 | 0.12 | 5.20 | 0.99 | <0.01 |
| October 2002 | 0.02 | 5.29 | 0.99 | <0.01 |
| January 2003 | 0.04 | 5.13 | 0.99 | <0.01 |
| April 2003 | 0.01 | 5.35 | 0.99 | <0.01 |
| June 2003 | 0.01 | 4.14 | 0.99 | <0.01 |
| **Mean ± SD** | **0.04 ± 0.05** | **5.02 ± 0.50** | | |
| | 2.0 km downstream of the WWTP input | | | |
| July 2002 | 1.05 | 4.94 | 0.99 | <0.01 |
| October 2002 | 1.18 | 4.67 | 0.98 | <0.01 |
| January 2003 | 1.17 | 4.37 | 0.99 | <0.01 |
| April 2003 | 1.18 | 5.65 | 0.99 | <0.01 |
| June 2003 | 0.50 | 4.49 | 0.99 | <0.01 |
| **Mean ± SD** | **1.02 ± 0.29** | **4.82 ± 0.51** | | |
| | 3.9 km downstream of the WWTP input | | | |
| July 2002 | 1.27 | 5.04 | 0.99 | <0.01 |
| October 2002 | 1.13 | 5.02 | 0.99 | <0.01 |
| January 2003 | 1.29 | 4.73 | 0.94 | <0.01 |
| April 2003 | 1.36 | 6.23 | 0.99 | <0.01 |
| June 2003 | 0.60 | 5.17 | 0.99 | <0.01 |
| **Mean ± SD** | **1.13 ± 0.31** | **5.24 ± 0.58** | | |
| | 10.0 km downstream of the WWTP input | | | |
| July 2002 | 0.32 | 5.22 | 0.99 | <0.01 |
| October 2002 | 0.25 | 5.67 | 0.99 | <0.01 |
| January 2003 | 0.37 | 4.75 | 0.99 | <0.01 |
| April 2003 | 1.36 | 5.66 | 0.99 | <0.01 |
| June 2003 | 0.15 | 4.71 | 0.99 | <0.01 |
| **Mean ± SD** | **0.49 ± 0.50** | **5.20 ± 0.47** | | |
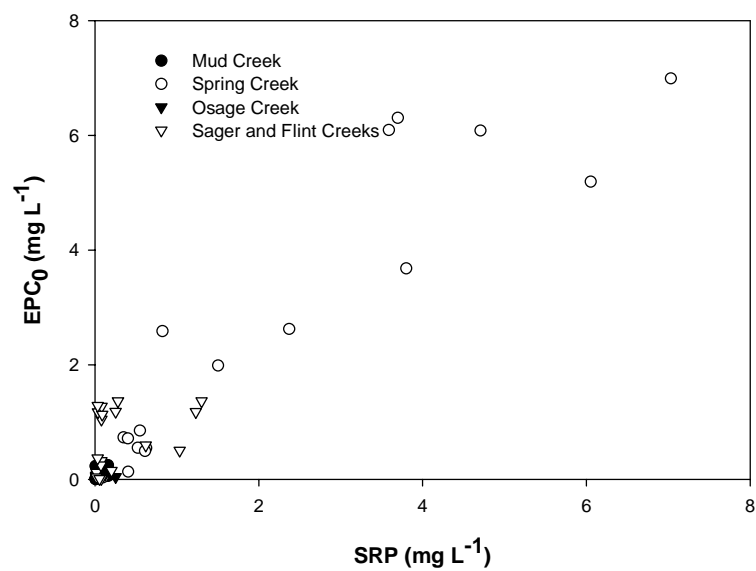
**Figure 4.8.** Correlation between water column soluble reactive P (SRP) and equilibrium P concentration (EPC$_0$) across all streams.

Sediment-P buffering capacity

The ability of the sediments to buffer P from the water column was evaluated using two different measures: k and PSI. k is the slope of the line used to estimate sediment $EPC_0$ and represents the quantity of P sorbed per unit increase in initial P concentration in those sediment extractions. PSI is a single point measure of the sediments ability to adsorb P (see methods). Greater PSI or k values indicate that sediments have a greater ability to adsorb P; i.e., higher buffering capacity.

The ability of benthic sediments to adsorb or buffer P loads decreased downstream from the WWTPs compared to upstream conditions. These sediment measures (k and PSI) were significantly greater (paired t-test for ln transformed data, $p<0.10$) upstream from the WWTP compared to values observed at the first site downstream across all streams (Tables 4.10 to 4.13 for k and Table 4.14 for PSI), except at Spring Creek and Sager/Flint Creeks, where k was not different. PSI values remained consistently less at the further downstream sites from the WWTP compared to upstream conditions and displayed no gradients with increasing distance downstream from the WWTP. At Mud Creek, Spring Creek, and Osage Creek, k was also consistently less at the other downstream sites compared to reference conditions whereas at Sager/Flint Creeks there were no significant differences. Similar to PSI, there were no definite patterns in k with increasing distance downstream from the WWTP across all streams. At the reference sites, benthic sediments at Mud Creek had a greater P buffering capacity (PSI) than the others, whereas the other streams had relatively similar ability to buffer P. However, there were few differences in P buffering capacity between sites and among streams downstream from the WWTP input. These results directly support the hypothesis that the WWTP effluent discharge have enriched stream sediments with P, and this observation was similar to previous work at WWTP enriched streams (Dorioz et al., 1998; Haggard et al., 2001a).

**Table 4.14** Phosphorus sorption index (PSI) or P buffering ability of sediments

| Date sampled | Site | Phosphorus Sorption Index | | | |
| --- | --- | --- | --- | --- | --- |
| | | Mud Creek | Spring Creek | Osage Creek | Sager/Flint Creeks |
| Jul 2002 | Upstream | 33.17 | 4.90 | 5.56 | 4.80 |
| Oct 2002 | Upstream | 10.34 | 4.42 | 5.61 | 4.65 |
| Jan 2003 | Upstream | 6.64 | 3.97 | 4.65 | 4.05 |
| Apr 2003 | Upstream | 7.01 | 5.78 | 5.01 | 5.66 |
| Jun 2003 | Upstream | 7.23 | 4.72 | 5.07 | 11.09 |
| **Mean ± SD** | | **12.88 ± 11.44** | **4.76 ± 0.47** | **5.18 ± 0.54** | **6.05 ± 2.88** |
| Jul 2002 | 1st Downstream | 2.86 | 2.62 | 3.79 | 4.18 |
| Oct 2002 | 1st Downstream | 4.07 | 1.42 | 5.05 | 2.57 |
| Jan 2003 | 1st Downstream | 2.93 | 2.62 | 3.65 | 2.02 |
| Apr 2003 | 1st Downstream | 2.96 | 2.61 | 4.29 | 3.22 |
| Jun 2003 | 1st Downstream | 3.38 | 3.18 | 4.34 | 4.18 |
| **Mean ± SD** | | **3.24 ± 0.51** | **2.49 ± 0.65** | **4.23 ± 0.77** | **3.23 ± 0.96** |
| Jul 2002 | 2nd Downstream | 5.04 | 1.17 | 3.45 | 3.34 |
| Oct 2002 | 2nd Downstream | 6.83 | 3.05 | 4.15 | 3.66 |
| Jan 2003 | 2nd Downstream | 3.08 | 0.07 | 4.14 | 1.74 |
| Apr 2003 | 2nd Downstream | 3.10 | 2.58 | 4.44 | 2.81 |
| Jun 2003 | 2nd Downstream | 3.26 | 3.39 | 3.97 | 3.73 |
| **Mean ± SD** | | **4.26 ± 1.65** | **2.05 ± 1.39** | **4.03 ± 0.40** | **3.06 ± 0.82** |
| Jul 2002 | 3rd Downstream | 2.89 | 2.92 | 4.56 | 3.90 |
| Oct 2002 | 3rd Downstream | 2.71 | 1.49 | 3.61 | 3.98 |
| Jan 2003 | 3rd Downstream | 2.90 | 1.85 | 4.20 | 3.14 |
| Apr 2003 | 3rd Downstream | 2.87 | 2.80 | 4.15 | 3.30 |
| Jun 2003 | 3rd Downstream | 3.40 | 3.18 | 3.74 | 3.79 |
| **Mean ± SD** | | **2.95 ± 0.26** | **2.45 ± 0.73** | **4.05 ± 0.48** | **3.62 ± 0.38** |

Exchangeable P

The later half of my first objective and part of third objective was to compare the sediment-P properties at sampling sites upstream and downstream from the WWTP inputs, based on the hypothesis that WWTP inputs have elevated sediment-bound P in these Ozark streams. Exchangeable P (EXP) is the loosely bound or easily available P for release from the sediments. EXP is a very conservative estimate of loosely bound P and should only be used to make relative comparisons among sites and streams.

EXP was significantly greater (paired t-test for ln transformed data, $p < 0.10$) at the first sites downstream from the WWTP compared to values at the upstream sites across all streams (Figure 4.9). EXP values remained consistently greater at sites further downstream from the WWTP compared to upstream conditions across all streams. With individual streams, EXP showed moderate decrease at the most downstream site at Mud Creek, whereas a substantial decrease was observed at the most downstream site of Sager/Flint Creeks, likely related to the availability of dissolved P in the water column. There was a sharp decrease in SRP concentrations because of dilution downstream from the confluence of Sager and Flint Creeks. EXP was still greater at the most downstream sites than that observed at the upstream sites across all streams.

An increase in EXP in the benthic sediments downstream from the WWTPs is second line of evidence that clearly supports the hypothesis that WWTP inputs have elevated the sediment-bound P in these Ozark streams. These results are also consistent with previous studies where EXP increased substantially in stream sediments below a municipal WWTP input (House and Denison, 1998; Dorioz et al., 1998; Haggard et al., 2001a). This observation also suggests that the sediments may represent a significant transient storage pool of available P in these streams.
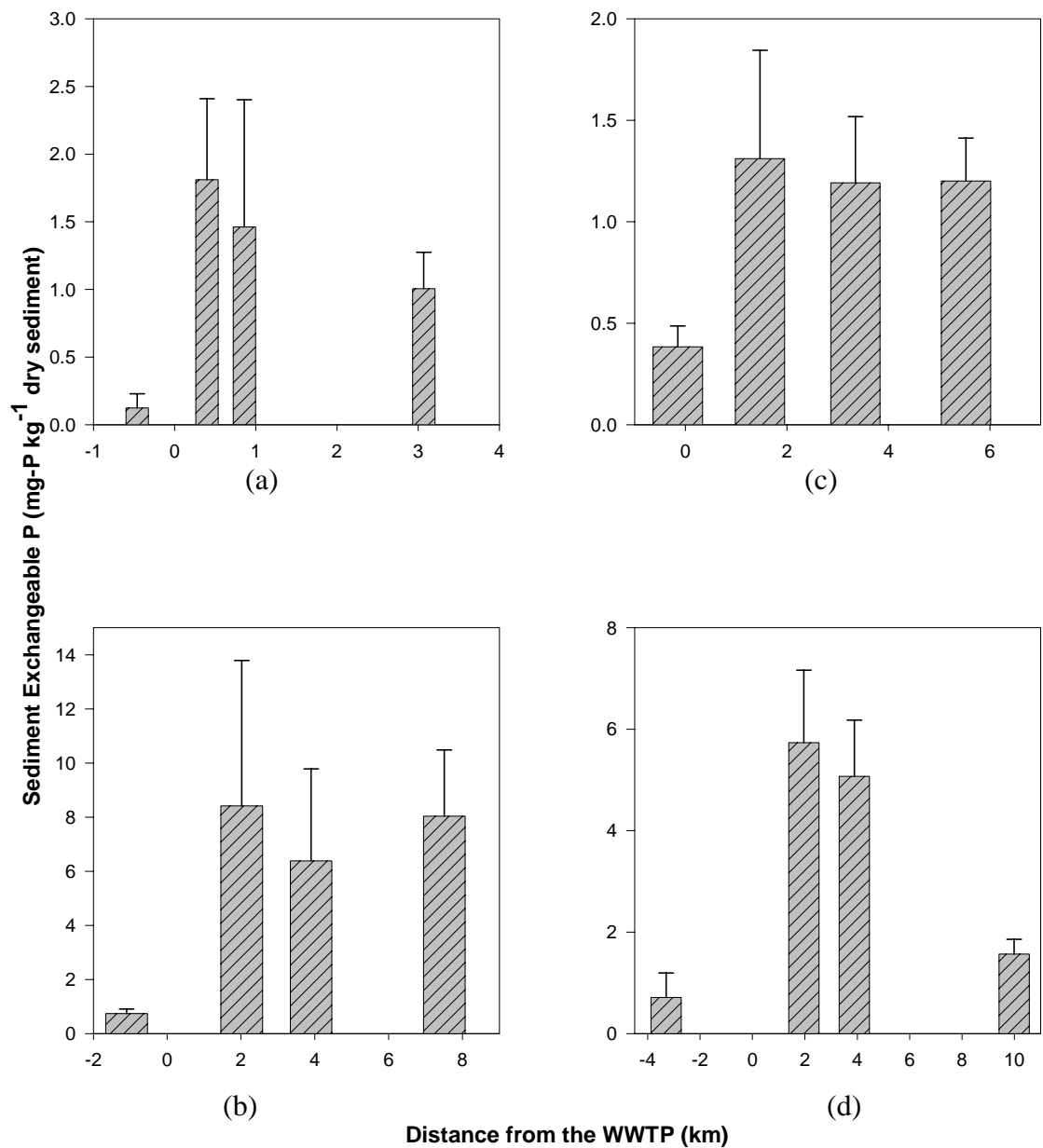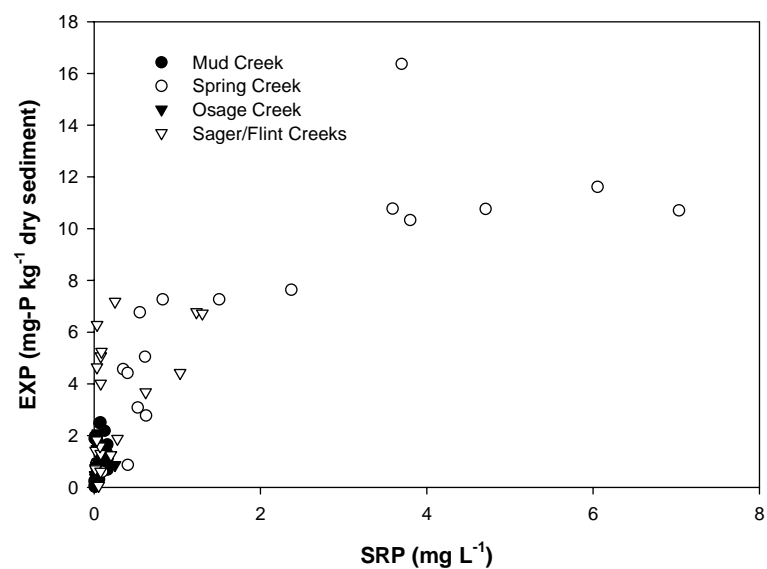
**Figure 4.9.** Easily exchangeable P (EXP) at: (a) Mud Creek (b) Spring Creek (c) Osage Creek, and (d) Sager/Flint Creeks upstream and downstream of the municipal WWTP.

The increase in EXP among these streams at the first site downstream from the WWTP input was greatest at Spring Creek (about 8.4 mg-P kg$^{-1}$ dry sediment) followed by Sager/Flint Creeks, Mud Creek and Osage Creek. Increases in EXP were consistent with increasing SRP concentrations at these streams. It is obvious that an increase in SRP concentrations downstream from the WWTP inputs provide large amount of dissolved P available for sediment sorption, thus increasing EXP in sediments. A strong correlation existed between SRP concentrations and the EXP in sediments at these streams (Figure 4.10, simple linear regression for ln transformed data, $R^2$=0.91, p<0.01, ln EXP=0.64 ln SRP + 1.54), providing further evidence that water column P influences sediment-bound P. The increase in SRP concentrations and EXP downstream from WWTP inputs creates large pools of dissolved inorganic P, and sediments may continuously adsorb and then release this easily exchangeable P to maintain equilibrium with the water column. A strong correlation was also observed between EXP and $EPC_0$ across all streams (Figure 4.11, simple linear regression for ln transformed data, $R^2$=0.94, p<0.01, ln $EPC_0$=1.42 ln EXP – 2.10).

Overall, the sediment-P results suggest that benthic sediments are an important temporary storage pool of P, possibly retaining and releasing P in stream ecosystems depending on water column P concentration. Therefore, these different small-scale investigations supported the important role of sediments in P retention in these Ozark streams. The results are in agreement with previous studies, where sediment sorption has played a major role in stream P retention (e.g., Dorioz et al., 1998; House and Warwick, 1999).

**Figure 4.10.** Relationship between soluble reactive P (SRP) concentrations and easily exchangeable P (EXP) across all streams.



**Figure 4.11.** Relationship between easily exchangeable P (EXP) and equilibrium P concentrations ($EPC_0$).

# SUMMARY AND CONCLUSIONS

The Illinois River that flows from Northwest Arkansas into northeast Oklahoma has aesthetic and recreational value and is listed as a Scenic River in Oklahoma. Point sources, especially municipal wastewater treatment plants (WWTPs) are still a significant source of P loading in headwater streams of the Illinois River, Northwest Arkansas (Haggard et al., 2003). Therefore, the overall goal of this study was to evaluate whole-stream P retention in four Ozark streams (Mud Creek, Spring Creek, Osage Creek, and Sager/Flint Creeks) receiving effluent from municipal WWTPs with varying degrees of P enrichment. The specific objectives were:

(1) To compare the SRP concentrations in the water column and stream sediments between reference sites (upstream) and sites downstream from the WWTP inputs;

(2) To examine longitudinal variation in SRP and $Cl^-$ concentrations (if any) downstream of WWTP inputs to determine if assimilation rather than dilution is responsible for net P retention;

(3) To conduct smaller-scale investigations to evaluate the ability of sediments to adsorb or release P by measuring easily exchangeable P (EXP), P sorption index (PSI), and equilibrium P concentration ($EPC_0$) in benthic sediments.

These objectives were based on the hypothesis that (1) P enrichment due to effluent from municipal WWTPs in headwater streams of the Illinois River has caused elevated water column soluble reactive P (SRP) and sediment-bound P in these stream ecosystems; (2) dilution due to groundwater and lateral contributions, and not assimilation is responsible for decreasing SRP concentration longitudinally downstream; and (3) the relationship between water column SRP and sediment-bound P are the controlling mechanisms of P concentrations in stream systems.

Elevated SRP concentrations at sites downstream from the WWTP input support the hypothesis that effluent discharge from the municipal WWTPs in Northwest Arkansas have enriched the receiving stream systems with P. In addition, an increase in sediment-bound P (EXP and $EPC_0$) and reduced ability of sediments to remove P from the water column is another line of evidence supporting the hypothesis of P enrichment from WWTPs. Elevated sediment-bound P and water column SRP demonstrate the profound impact of WWTPs on services provided by these stream ecosystems, such as nutrient assimilation (Costanza et al., 1998).

Results indicated that at Spring and Sager/Flint Creeks dilution due to groundwater and lateral contributions was responsible for decline in SRP concentrations longitudinally, downstream from the WWTP input. Long net uptake lengths ($S_{net}$) estimated up to 43 km suggest low net P retention efficiency of these stream ecosystems. The significant negative $S_{net}$ that was common in this study indicated a P release from the sediments into the water column. It is noteworthy that the negative $S_{net}$ at Spring Creek occurred on sampling dates after November 2002 when P concentrations in the effluent were probably less than sediment $EPC_0$ and sediments became a potential P source. However, this is not surprising, since this WWTP has been making voluntary efforts to reduce P in its effluent.

The EPC$_0$ was strongly correlated with water column SRP across all streams suggesting that any changes in P from source i.e., WWTPs could alter this relationship, and either initiate a release or adsorption of P by stream sediments. However, at different sites the sediments were either in equilibrium with water column SRP, acting as a conduit to transport P, or behaved as a source or sink of P. Thus, sediments most likely played an important role in regulating the SRP concentrations in water column in these Ozark streams. These sediments can thus act as a potential P source, maintaining elevated water column SRP even if the municipal WWTPs will reduce the P concentration in the effluent.

The water column SRP and sediment-bound P in WWTP impacted streams may reduce temporally, however, it is difficult to predict a definite time-period. It may be a few years that self-purifying capacity of streams will reduce P concentrations below eutrophic levels. The recovery rate of these aquatic ecosystems will depend on loading from municipal WWTPs, amount of sediment transported or retained, and distance between other P inputs. The most important factor will be of in-stream uptake capacity by both abiotic and biotic components.

Municipal WWTPs are still a significant source of phosphorus (P) loading in the headwater streams of Northwest Arkansas and have significantly altered the P transport and retention in these streams. This study demonstrated the complexity of managing and maintaining the critical in-stream ecological service of nutrient cycling.

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**ILLINOIS RIVER**
**2002 POLLUTANT LOADS**
**AT ARKANSAS HIGHWAY 59 BRIDGE**

Submitted to the
Arkansas Soil and Water Conservation Commission
and the
Arkansas-Oklahoma Arkansas River Compact Commission

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## SUMMARY

Results for Illinois River at AR59 for calendar year **2002**.

| Pollutant | Total Discharge (m³/yr) | Total Load (kg/yr) | Average Discharge (m³/s) | Mean Concentrations (mg/l) |
|---|---|---|---|---|
| | 531,000,000 | | 16.8 | |
| N03-N | | 1,340,000 | | 2.52 |
| TKN | | 294,000 | | 0.55 |
| TP | | 218,000 | | 0.41 |
| TSS | | 38,900,000 | | 73 |

- Comparison between the loads and discharge calculated for 2002 to previous years indicate a decline in all parameters.

Comparison between 1997, 1998, 1999, 2000,2001 and 2002 **loads**.

| Parameter | **1997** Loads | **1998** Loads | **1999** Loads | **2000** Loads | **2001** Loads | **2002** Loads |
|---|---|---|---|---|---|---|
| Discharge (m³) | 458,460,000 | 588,000,000 | 635,000,000 | 536,000,000 | 532,000,000 | 531,000,000 |
| N03-N (kg/yr) | 1,020,000 | 1,390,000 | 1,560,000 | 1,100,000 | 1,520,000 | 1,340,000 |
| TKN (kg/yr) | 301,000 | 481,000 | 514,000 | 462,000 | 447,000 | 294,000 |
| TP (kg/yr) | 127,000 | 232,000 | 267,000 | 283,000 | 256,000 | 218,000 |
| TSS (kg/yr) | 18,400,000 | 72,600,000 | 77,100,000 | 63,600,000 | 70,800,000 | 39,000,000 |

- A total of 56 water samples were collected and analyzed in 2002.

- All significant storm events were sampled during the year.

- Total Phosphorus loads are trending down.

## INTRODUCTION

Automatic water samplers and a U. S. Geological Survey gauging station were established in 1995 on the main stem of the Illinois River at the Arkansas Highway 59 Bridge.  Since that time, continuous stage and discharge measurements and water quality sampling have been used to determine pollutant concentrations and loads in the Arkansas portion of the Illinois River. This report represents the results from the measurement and sampling by the Arkansas Water Resources Center -Water Quality Lab for January 1, 2002 to December 31, 2002.

## PREVIOUS RESULTS

In the fall of 1995, a gauge was installed at the Highway 59 Bridge by the USGS and automatic sampling equipment was installed by the Arkansas Water Resource Center. In September 1995, sampling was begun on the Illinois River. Grab samples were taken every week and storms were sampled using an automatic sampler set to take samples every 4 hours.  During the period from September 13, 1995 to September 15, 1996 one hundred thirty seven grab samples and discrete storm samples were collected and analyzed. Table 1 summarizes the results from that study (Parker et al, 1997).

Table 1. Results from **1996** study period (Parker et al, 1997).

| Nutrients | Total Discharge (m$^3$/yr) | Total Load (kg/yr) | Average Discharge (m$^3$/s) | Average Flow Weighted Concentrations (mg/l) |
|---|---|---|---|---|
| | 300,775,680 | | 9.5 | |
| N03-N | | 550,000 | | 2.0 |
| NH3-N | | 8,530 | | 0.031 |
| TKN | | 201,000 | | 0.74 |
| TP | | 89,900 | | 0.29 |
| TSS | | 27,000,000 | | 89 |
| TOC | | 1,130,000 | | 4.2 |

Sampling was discontinued on September 15, 1996 and no water quality samples were taken between September 15, 1996 and November 1, 1996. Stage and discharge was still recorded for this period, however, no loads were calculated. Water quality sampling was resumed on November 1, 1996. The sampling protocol was changed to collection of grab samples every two weeks and flow-weighted storm composite samples.  Between November 1, 1996 and December 31, 1996 a total of four grab samples and one storm composite sample were collected and analyzed. Stage and discharge were recorded.

During the period from January 1, 1997 to October 15, 1997, there were twenty-six grab samples and twenty-five storm composite samples collected and analyzed using the same protocol. During the period from October 15, 1997 to December 31, 1997, the sampling protocol was changed to taking grab samples every two or three days and taking discrete storm samples every thirty or sixty minutes. In this period, there were twenty-four grab samples and one hundred and forty storm discrete samples collected and analyzed. The loads and mean concentrations for 1997 calculated using these samples are summarized in Table 2.

Table 2. Results from **1997**-study period (Nelson and Soerens, 1998).

| Pollutant | Total Discharge (m$^3$/yr) | Total Load (kg/yr) | Average Discharge (m$^3$/s) | Mean Concentrations (mg/l) |
|---|---|---|---|---|
| | 458,460,000 | | 14.5 | |
| N03-N | | 1,020,000 | | 2.24 |
| TKN | | 301,000 | | 0.66 |
| TP | | 127,000 | | 0.28 |
| TSS | | 18,400,000 | | 40.2 |

In the periods from January 1, 1998 to May 15, 1998 and November 1, 1998 to December 31, 1998, the Illinois River sampling was supplemented by sampling from another research project. That project, sponsored by the USGS Water Resource Institute Program, was titled "Investigation of Optimum Sample Interval for Determining Storm Water Pollutant Loads" by Marc Nelson, Thomas Soerens and Jean Spooner. The sampling protocol for that project consisted of taking grab samples every two days and discrete storm water samples at thirty-minute intervals on the rising limb and sixty-minute intervals on the falling limb of storm hydrographs. Storm water sampling was begun at a variable trigger level set to the current stage plus ten percent and adjusted every two days. After the first thirty-six hours of each storm, sample times were increased to from four to twenty-four hours until the stage fell below the initial trigger. All samples were collected within twenty-four hours. All samples were analyzed for nitrate nitrogen (NO3-N), ammonia nitrogen (NH4-N), total Kjeldahl nitrogen (TKN), total phosphorus (TP), ortho phosphate (O-P) and total suspended solids (TSS). AWRC Field Services personnel collected all samples and all samples were analyzed by the AWRC Water Quality Lab using standard field and laboratory QA/QC procedures.

In the period from May 16, 1998 to October 31, 1998, the sampling protocol was changed back to the collection of grab samples every two weeks and flow-weighted composite samples during storms. Storms were defined as all flows above a five-foot trigger level. Once stage had risen above the trigger, a USGS programmable data logger began summing the volume of water discharged. Once a determined amount of water had been discharged, the data logger sent a signal to an automatic water sampler that filled one of twenty-four one-liter bottles. The total was then reset to zero and discharge was again summed for the next sample. In this fashion up to twenty-four samples, each representing an equal volume of storm water was collected. The volume of water represented by each individual sample was eight million cubic feet. These samples were retrieved before all twenty-four bottles were filled, or within 48 hours after being taken. The individual samples were composited into a flow-weighted composite storm sample by combining equal volumes of each. Samples were taken as long as the stage remained above the trigger level. All samples were analyzed for nitrate nitrogen (NO3-N), total Kjeldahl nitrogen (TKN), total phosphorus (TP) and total suspended solids (TSS). AWRC Field Services personnel collected all samples and all samples were analyzed by the AWRC Water Quality Lab using standard field and laboratory QA/QC procedures.

In the period from January 1, 1998 to December 31, 1998, there were four hundred and forty nine samples collected and analyzed. These results are summarized in Table 3.

Table 3. Results from **1998**-study period (Nelson and Soerens, 1999).

| Pollutant | Total Discharge (m$^3$/yr) | Total Load (kg/yr) | Average Discharge (m$^3$/s) | Mean Concentrations (mg/l) |
|---|---|---|---|---|
| | 588,000,000 | | 18.6 | |
| N03-N | | 1,390,000 | | 2.37 |
| TKN | | 481,000 | | 0.82 |
| TP | | 232,000 | | 0.39 |
| TSS | | 72,600,000 | | 123.5 |

In the period from January 1, 1999 to December 31, 1999, there were three hundred and sixty nine samples collected and analyzed. These results are summarized in Table 4.

Table 4. Results from the **1999** study period (Nelson and Soerens, 2000).

| Pollutant | Total Discharge (m³/yr) | Total Load (kg/yr) | Average Discharge (m³/s) | Mean Concentrations (mg/l) |
|---|---|---|---|---|
| | 635,000,000 | | 20.0 | |
| N03-N | | 1,560,000 | | 2.45 |
| TKN | | 514,000 | | 0.81 |
| TP | | 267,000 | | 0.42 |
| TSS | | 77,100,000 | | 121 |

In the period from January 1, 2000 to December 31, 2000, there were fifty-one samples collected and analyzed. These results are summarized in Table 5.

Table 5. Results for Illinois River at AR59 for Calendar Year **2000**. (Nelson and Soerens, 2001).

| Pollutant | Total Discharge (m³/yr) | Total Load (kg/yr) | Average Discharge (m³/s) | Mean Concentrations (mg/l) |
|---|---|---|---|---|
| | 536,000,000 | | 17 | |
| N03-N | | 1,100,000 | | 2.06 |
| TKN | | 462,000 | | 0.86 |
| TP | | 283,000 | | 0.53 |
| TSS | | 63,600,000 | | 118 |

In the period from January 1, 2001 to December 31, 2001, there were forty-nine samples collected and analyzed. These results are summarized in Table 6.

Table 6. Results for Illinois River at AR59 for Calendar Year **2001**. (Nelson and Soerens, 2002).

| Pollutant | Total Discharge (m³/yr) | Total Load (kg/yr) | Average Discharge (m³/s) | Mean Concentrations (mg/l) |
|---|---|---|---|---|
| | 532,000,000 | | 16.9 | |
| N03-N | | 1,520,000 | | 2.86 |
| TKN | | 447,000 | | 0.84 |
| TP | | 256,000 | | 0.48 |
| TSS | | 70,800,000 | | 133 |

METHODS

In the period from January 1, 2002 to December 31, 2002, the Illinois River sampling followed the following protocol. Base flow grab samples were taken every two weeks using the automatic sampler. Storm flow-weighted composite samples were taken during all storm events. Sampling was initiated when the river stage exceeded the trigger level of 5 feet.  Flow-weighted composite samples were taken by causing the sampler to collect a single discrete sample for every four million cubic feet of water that passed the bridge. These discrete samples were collected once per day and composited by taking equal volumes from each discrete and combining them to form a single sample. Flow-weighted composite samples were taken from trigger level to trigger level of all storm events where the river stage was above the trigger for at least twelve hours. All samples were collected within twenty-four hours of being taken.  All samples were analyzed for nitrate nitrogen (NO3-N), ammonia nitrogen (NH4-N), total Kjeldahl nitrogen (TKN), total

phosphorus (TP), ortho-phosphate (O-P) and total suspended solids (TSS). AWRC Field Services personnel collected all samples and all samples were analyzed by the AWRC Water Quality Lab using standard field and laboratory QA/QC procedures.

Calendar year pollutants loads and mean concentrations were calculated from the collected data. USGS stage and discharge data in thirty-minute intervals was used to calculate thirty-minute total volumes. Each volume was assigned a pollutant concentration. The pollutant concentrations were assigned by applying the results of grab samples between storm trigger levels and the results of storm water samples above trigger levels. All concentration data were assigned to the time periods from half way to the previous sample to half way to the subsequent sample except the first and last of a storm or base flow period which were assigned to the start or end of the period. Thirty-minute loads were calculated by multiplying thirty-minute volumes by their assigned concentrations. The yearly loads were calculated by summing the thirty-minute loads during the calendar year. Yearly mean concentrations were calculated by dividing the yearly load by the yearly volume.

In addition to the above sampling for load determination, the AWRC in conjunction with the USGS conducted cross-section sampling to determine the relationship between auto-sampler concentrations and cross-section concentrations. The USGS collected evenly weighted integrated (EWI) cross section samples at the same time AWRC collected discrete auto-samples. All samples were transported and analyzed by the AWRC Water Quality Lab. Five storm-flow paired samples were taken and compared during the year.

RESULTS

In the period from January 1, 2002 to December 31, 2002, there were twenty-five composite storm samples and twenty-six base-flow grab samples collected, analyzed and used to calculate loads. These results are summarized in Table 7 and Figure 1.

Table 7. Results for Illinois River at AR59 for Calendar Year **2002**.

| Pollutant | Total Discharge (m$^3$/yr) | Total Load (kg/yr) | Average Discharge (m$^3$/s) | Mean Concentrations (mg/l) |
|---|---|---|---|---|
|  | 531,000,000 |  | 16.8 |  |
| N03-N |  | 1,340,000 |  | 2.52 |
| TKN |  | 294,000 |  | 0.55 |
| TP |  | 218,000 |  | 0.41 |
| TSS |  | 38,900,000 |  | 73 |

Figure 1. Recorded stage and measured concentration for 2002.



**ILLINOIS RIVER
HIGHWAY 59
2002**
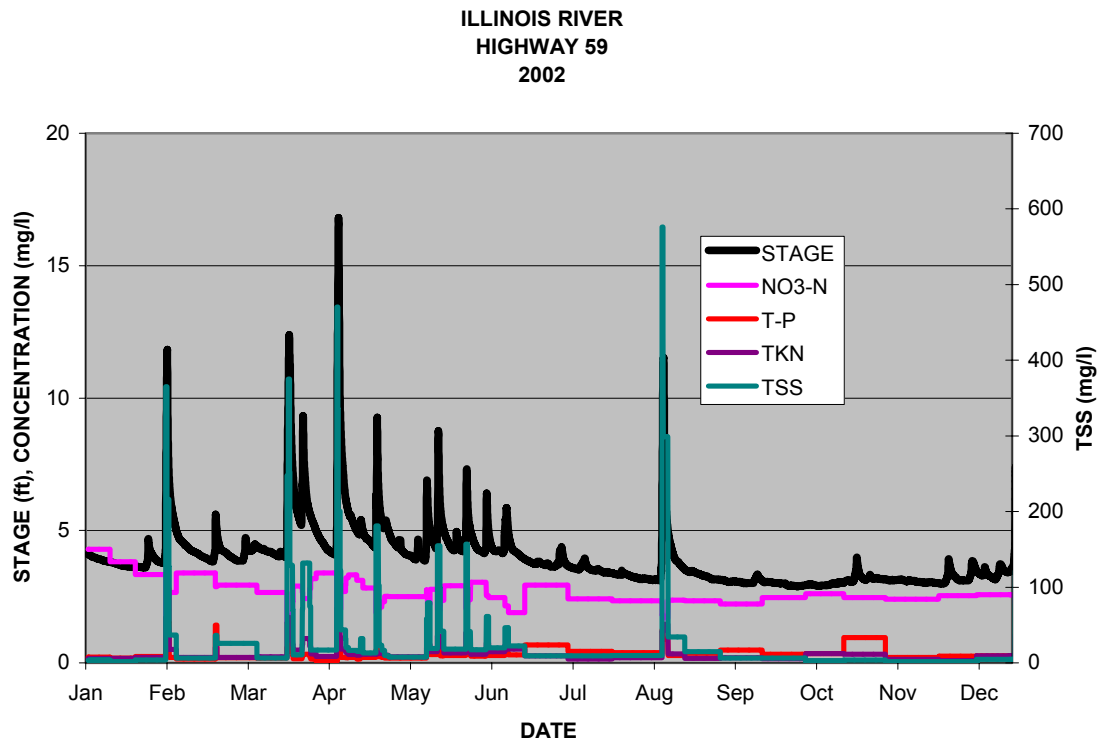
Figure 2. Trends in mean discharge and mean concentrations.
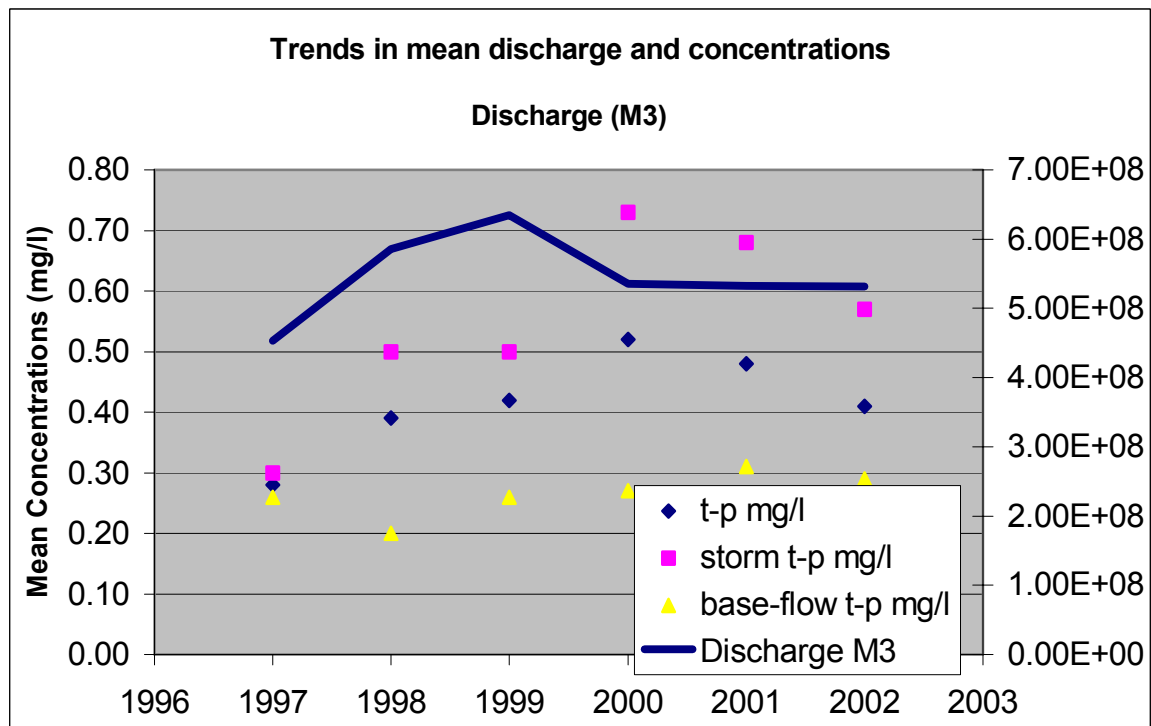
Figure 3. Trends in discharge and loads.



**Trends in discharge and loads**

Legend:
- T-P kg
- Storm T-P kg
- Base T-p kg
- Discharge M3
- storm discharge M3
- base discharge M3
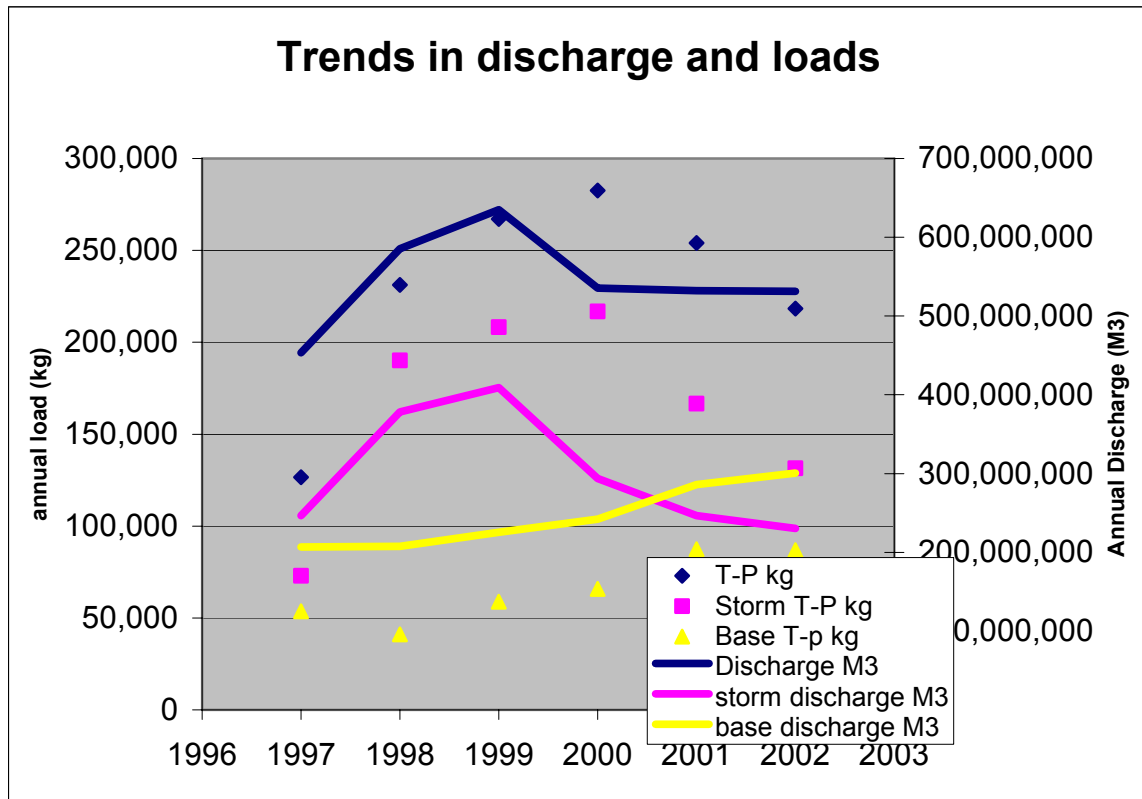
Figure 4. Regression of log TSS concentrations AWRC vs. USGS.



**Comparison between USGS and AWRC TSS**

$y = 0.9332x$
$R^2 = 0.6855$

Legend:
- log awrc-tss
- Linear (log awrc-tss)
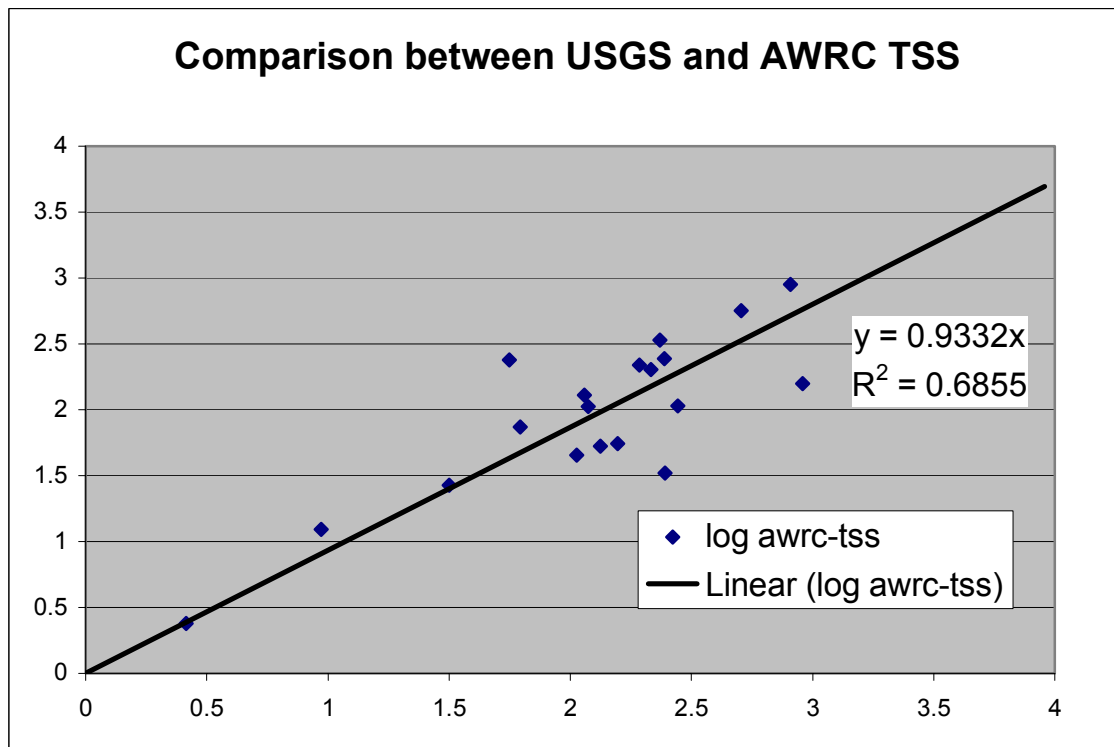
Figure 5. Regression of log T-P concentrations AWRC vs. USGS.



**Comparison between USGS and AWRC T-P**

$y = 1.0999x$
$R^2 = 0.6686$

- ◆ log awrc-tp
- — Linear (log awrc-tp)
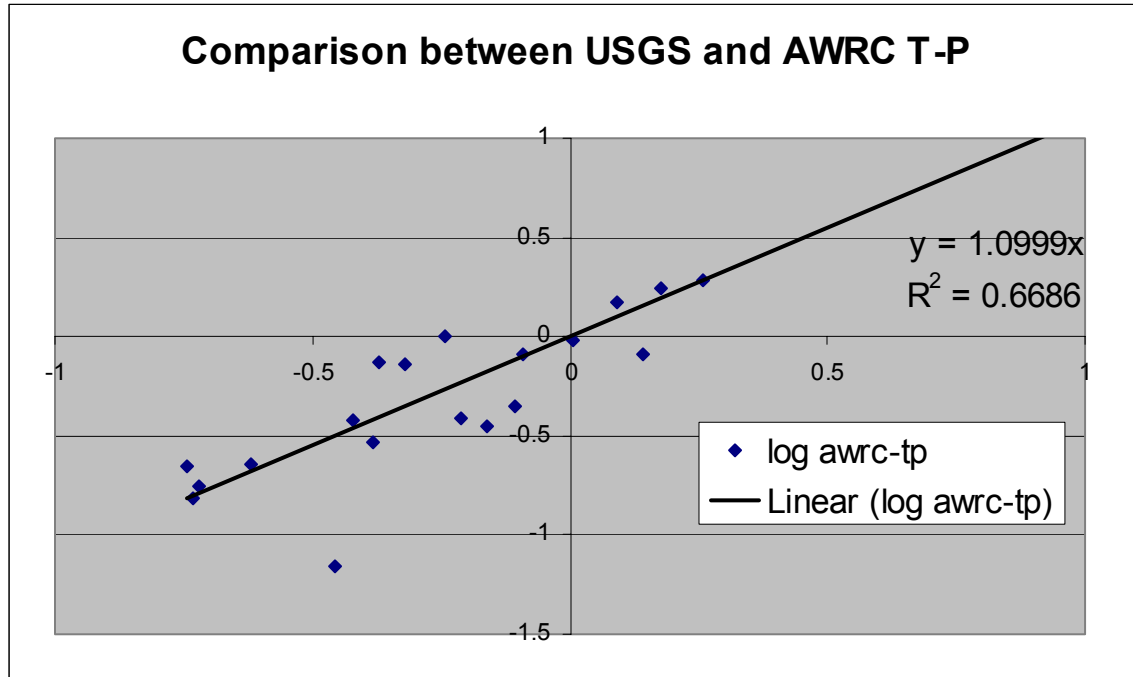
DISCUSSION

The loads that were calculated for the year 2002 should be considered a very reliable estimate of the actual loads in the Illinois River in Arkansas. There were no gaps in the discharge data and all storm events were sampled adequately.

A source of error in the use of automatic samplers to collect samples is that the sampler may take samples that are not representative of the cross-section. In an effort to determine the possible error, beginning in 1998, the USGS began taking samples that represent the entire cross-section (EWI samples) at the same time the auto sampler was taking samples. Results from those samples indicate that the auto samples may be underestimating TSS by 7% and overestimating concentrations of total phosphorus by 10% (see Figure 4 and 5) compared to the USGS EWI samples. Figures 4 and 5 indicate that this relationship is not consistent. This may be a result of not sampling at exactly the same time during a period when concentrations are changing rapidly.

Results from six years water quality monitoring for total phosphorus are summarized in Figures 2 and 3. The mean concentrations were determined by dividing the annual load by the annual discharge. Shown are the base flows, storm flows and combined concentrations. Base flow concentrations represent the phosphorus load determined when the river stage was below five feet divided by the total discharge that occurred when the river stage was below five feet. Storm flow concentrations are loads divided by discharge above five feet. The combined flow concentration is the total load divided by the total discharge. These results show a relatively flat to slightly increasing trend in base flow concentrations.

Storm flow concentrations tend to be related to discharge, with higher concentrations associated with higher discharges. For the first three years of the study, this relationship was observed. The fourth year (2000) showed discharge continuing to rise while storm concentration fell and subsequent years showed a decreasing trend in storm flow concentrations while discharge remained fairly constant. This may indicate that non-point source phosphorus impacts have begun to decrease after reaching a peak in 2000. Short-term trends in total phosphorus loads show the impacts of changing storm water concentrations as shown in figure 7. For the first 3 years of the study, the annual loads were increasing at a rate of approximately 70,000 kg per year. The loads decreased at a rate of approximately 30,000 kg per year for the last three years. These are short-term trends that may be more indicative of trends in runoff and not long-term impacts.

Figure 6. Short-term trends in T-P loads.
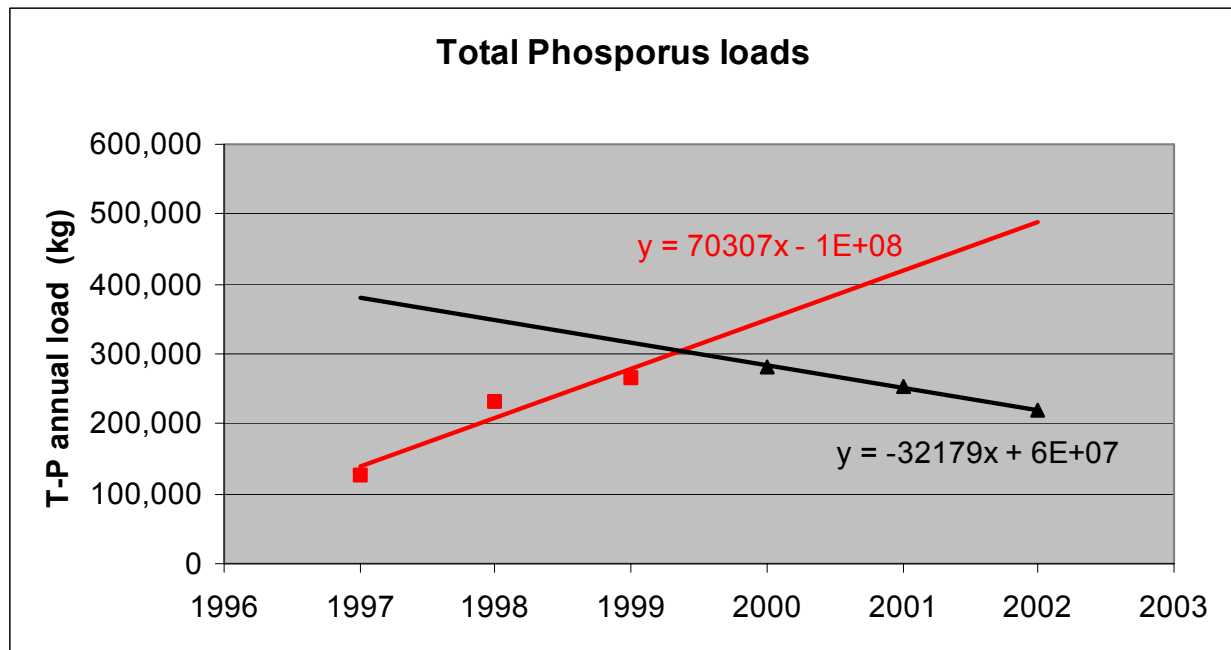


The loads and concentrations developed for the Illinois River can be compared to loads and concentrations developed in other watersheds in Northwest Arkansas. Five other watersheds have been monitored using the same monitoring and load calculation protocols. The only differences between the protocols are that trigger levels and storm composite sample volumes are different for each site. This means that the distinction between storm and base flows (defined here as the trigger level) may be relatively different at each site.

The results for the six watersheds are summarized in Table 8 and Figure 7. The table and figure show TSS and phosphorus as total annual loads per watershed acre, as storm loads per watershed acre and as base-flow concentrations. Normalizing total and storm loads to a per acre basis allows easy comparison between watersheds of differing sizes. The total loads indicate the mass of TSS or P that are being transported to a receiving water body. Storm loads per acre may be used to represent relative impacts from non-point sources. In Figure 8, a red line represents the total loads and blue diamonds represents the storm loads. The Illinois River watershed has relatively low total TSS compared to the others and most of the TSS is transported during storm events. The P load for the Illinois is fairly consistent with the other watersheds with Moores Creek (a primarily agricultural sub-watershed of the Illinois) showing higher levels of P per acre especially during storm events and the Kings River showing significantly lower values.

The base-flow concentrations show relative levels of TSS and P that are impacting in-stream biological activity during most of the year. These are the values that are of greatest interest for determining impacts to in-stream macro invertebrate habitat and nuisance algae production. The Illinois River has low concentrations of TSS compared to the others, especially the White and it's sub-watershed the West Fork which was listed in the Arkansas 2000 303d list as impaired by turbidity. The base-flow P concentrations for all of the watersheds except the Moores Creek are similar. This is a possible confirmation that the base-flow concentrations are effected by wastewater treatment plant discharges, as Moores Creek is the only watershed without a permitted WWTP discharge.

Table 8. Comparison of six watersheds.

|  | Illinois River@59 | White River@wyman | West Fork | Kings River@143 | Osage Creek@112 | Moores Creek |
|---|---|---|---|---|---|---|
| **ACRES** | 368,000 | 256,000 | 65,920 | 337,280 | 22,208 | 2,200 |
| **YEARS of data** | 6 | 1 | 1 | 4 | 1 | 2 |
|  |  |  |  |  |  |  |
| **TSS load (#/acre)** | 340 | 644 | 839 | 351 | 466 | 413 |
| **TSS load storm (#/acre)** | 312 | 475 | 570 | 320 | 182 | 382 |
| **TSS conc. base (mg/l)** | 20 | 93 | 170 | 27 | 39 | 12 |
| **P load (#/acre)** | 1.38 | 1.38 | 1.30 | 0.89 | 1.16 | 1.44 |
| **P storm load (#/acre)** | 0.98 | 1.00 | 0.91 | 0.62 | 0.70 | 1.16 |
| **P base conc. (mg/l)** | 0.26 | 0.21 | 0.25 | 0.24 | 0.28 | 0.10 |
| **DISCHARGE (ft3)** | 1.9E+10 | 1.5E+10 | 3.5E+09 | 1.5E+10 | 1.2E+09 | 8.6E+07 |
| **DISCHARGE/AC (ft3/acre)** | 52,625 | 57,847 | 53,419 | 44,161 | 55,475 | 38,987 |

Figure 7. Comparison of six watersheds.



**TSS Storm Loads per acre**

(Chart: Storm Loads (lbs per acre) vs. watershed. Y-axis 0 to 900.)

Illinois River@59, White River@wyman, West Fork, Kings River@143, Osage Creek@112, Moores Creek

**TSS mean concentration Base flow**

(Chart: Base flow concentration (mg/l) vs. watershed. Y-axis 0 to 180.)

Illinois River@59, White River@wyman, West Fork, Kings River@143, Osage Creek@112, Moores Creek

Figure 7. (continued)

**T-P Storm Loads per acre**



**T-P mean concentration Base flow**

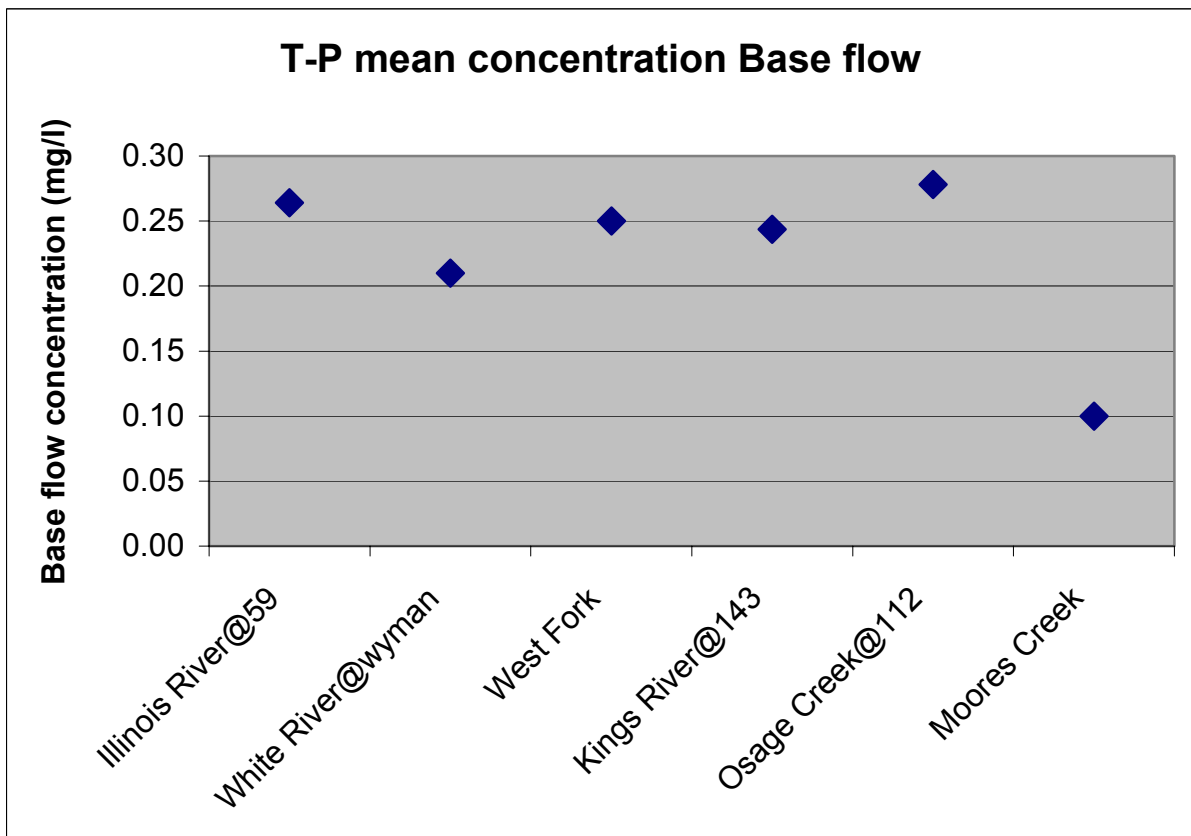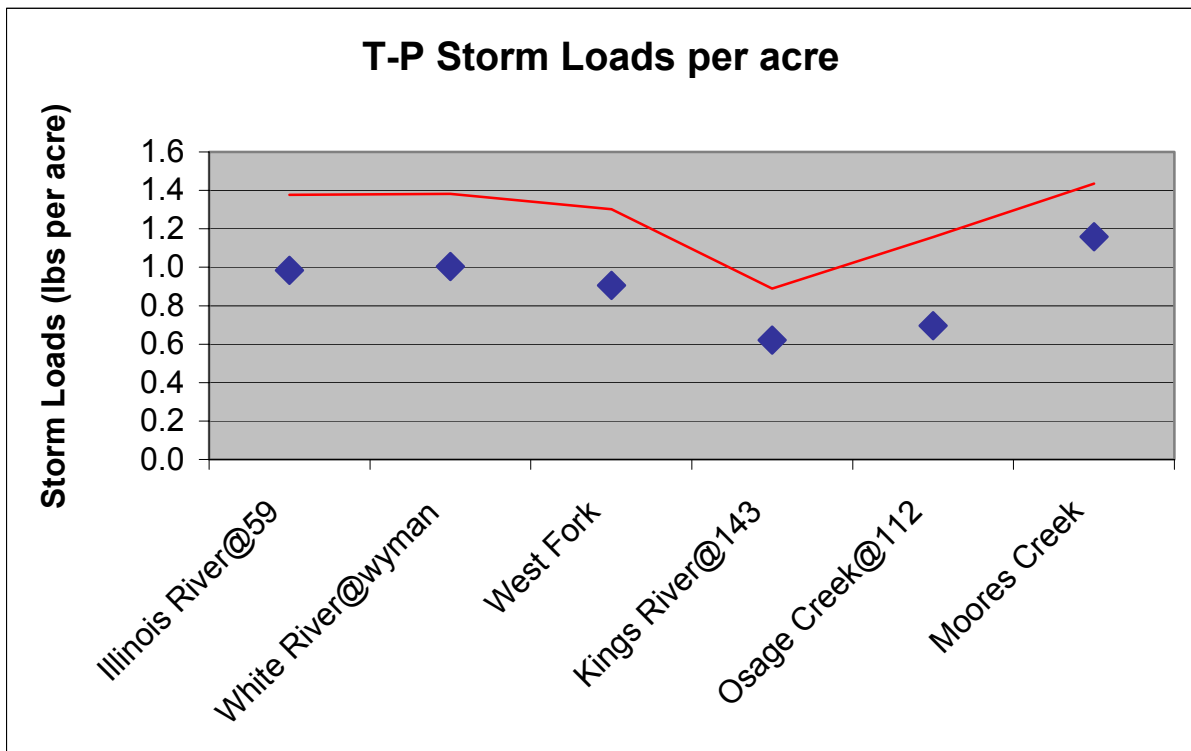**REFERENCES**

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